Digital technology used in the application of colour measurement and colour formulation of skin in maxillofacial prosthetics

Farah, Ariane

Awarding institution:
King's College London

DIGITAL TECHNOLOGY USED IN THE APPLICATION OF COLOUR MEASUREMENT AND COLOUR FORMULATION OF SKIN IN MAXILLOFACIAL PROSTHETICS

Ariane Farah

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Abstract

Statement of problem: Colour degradation and deterioration of mechanical properties of maxillofacial prostheses requires their frequent renewal; and the traditional trial and error method of colour matching natural skin with silicone elastomer is unpredictable and requires a more scientific approach.

Materials and methods: For colour stability and mechanical properties testing, M511 silicone was coloured with Spectromatch Pro colourants and stored in darkness, exposed to accelerated ageing and outdoor weathering. Test groups included non-pigmented, individually pigmented samples and Caucasian skin tone coloured specimens. Investigations further involved the use of UV-light absorbers and silicone surface sealants to improve the colour stability of elastomer. For assessment of the Spectromatch Pro colour formulation software in comparison with the traditional colour matching method, the same elastomer and colourants were utilised. Colour measurements of skin and elastomer were recorded utilising a spectrophotometer and mean colour differences ($\overline{\Delta E}$) were calculated based on the recorded L*a*b* values. All data was analysed using linear mixed models and Šídák's multiple comparison of means test ($\alpha = 0.05$).

Results: There was a significant effect of time and environment on colour and mechanical properties of elastomer ($p = 0.001$), apart from tear strength which was not significantly different. Greatest $\overline{\Delta E}$ were observed for specimens exposed to accelerated ageing. Caucasian skin coloured samples demonstrated $\overline{\Delta E}$ of 3.26; but application of a surface sealant with incorporated UV-light absorber improved its colour stability (1.56 $\overline{\Delta E}$). Use of the Spectromatch Pro colour formulation software resulted in better colour matching results than did the traditional method; with non-perceivable $\overline{\Delta E}$ of 0.79 for Afro/Afro-Caribbean subjects and perceivable but acceptable $\overline{\Delta E}$ of 1.46 for Caucasian skin tones.

Conclusions: M511 in conjunction with Spectromatch Pro colourants demonstrated good overall colour stability; and the Spectromatch Pro software

achieved best colour matching results and makes these systems suitable for daily clinical use.

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REVIEW OF LITERATURE

1.1. Introduction

The field of maxillofacial prosthetics is a small but specialised area and is concerned with anatomic functional or cosmetic reconstruction of maxillofacial defects by means of non-living substitutes in order to improve self-confidence and quality of life of patients (Bulbulian 1965; Chalian and Philips 1974; Lepley 1974; Thomas 2006).

The art and science of maxillofacial prosthetics has advanced as improved modern materials and fabrication methods became available. Today, silicone elastomers have replaced almost all of the materials that had been previously used (Conroy 1983; Conroy and Hulterstrom 1978; Lontz 1990). In maxillofacial prosthetic rehabilitation, silicone elastomer is individually coloured using pigments and flocking in order to establish a balanced colour match of elastomer with a patient's natural skin tone (Ma *et al*. 1988; Lontz 1990; Thomas 2006).

Regardless of which colouring system and technology is employed, one of the major problems encountered with facial appliances in clinical service is their alteration in colour and the deterioration of physical and mechanical properties of silicone elastomer over time. These changes have been attributed to a wide spectrum of environmental factors including UV-light, changes in humidity and temperature, air pollution, personal habits and practices of patients such as smoking and prosthesis cleaning regimens (Beatty *et al*. 1999; Lemon *et al.* 1995; Tran *et al.* 2004).

However, UV-light has been determined as one of the main causes resulting in colour changes of facial prostheses and attempts have been made to utilise UV-light absorbers in order to improve the colour stability of silicone elastomers and subsequently of facial prostheses; and some promising results have been reported (Bryant *et al.* 1994; Han *et al*. 2013; Kheur *et al*. 2016; Tran *et al*. 2004).

The traditional and currently most frequently applied method of colour matching involves the arbitrary trial and error approach but is dependent upon the expertise and skills of the clinician undertaking this procedure and therefore unreliable and its results unpredictable. The drawbacks of this method have been recognised and more recently, scientific technologies based upon computer enhanced systems have been utilised. Spectrophotometry in conjunction with colour formulation software has been used to establish skin colour formulae for maxillofacial applications. The aim is to turn the process of colour matching into a reliable and predictable method that also controls metamerism; the phenomenon wherein two colours having different spectral compositions match one another (Hunt and Pointer 2011).

This study has been designed to investigate the colour stability of pigments from a new colouring system in conjunction with a maxillofacial elastomer when exposed to various environmental conditions for a prolonged period of time. Further research has been conducted on whether the use of UV-light absorbers and a surface sealant will improve the colour stability of non-pigmented and pigmented maxillofacial elastomer.

The second part of this study was designed to investigate whether a recently introduced colour formulation system for maxillofacial applications improves the colour matching results between elastomer and natural skin when compared with the traditional method involving the arbitrary trial and error approach.

1.2. The art and science of maxillofacial prosthetics

The field of maxillofacial prosthetics is a small but specialised area and may be considered as an important adjunct of plastic and reconstructive surgery (Thomas 2006). It has been defined as the art and science of anatomic functional or cosmetic reconstruction by means of non-living substitutes for those regions in the maxilla, mandible and face that are missing or are defective because of surgical intervention, trauma, pathology, developmental or congenital malformations (Bulbulian 1965; Chalian and Philips 1974; Lepley 1974).

The maxillofacial environment is of crucial importance as it comprises of various functions including communication and mastication. The face in particular represents the primary mode of self-expression and is required for all interpersonal relationships (Bailey and Edwards 1975; Newton *et al*. 1999). Defects of the craniofacial region can be physically, socially and psychologically devastating for the afflicted individual and consequently, prosthetic treatment senses functional and aesthetic rehabilitation to improve self-confidence and quality of life of the patient, as well as to facilitate social reintegration (Frank 1975; Van Oort 1983).

The two main materials used when fabricating facial prostheses are silicone elastomers and colourants where the silicone is custom coloured with pigments in order to achieve a natural looking colour blend between the prosthesis and surrounding natural skin.

1.3. Traditional method of fabricating a facial prosthesis

The traditional method of manufacturing a maxillofacial prosthesis is performed in several steps and summarised in Table 1.1 (Thomas 1994 and 2006).

PATIENT ASSESSMENT	➢ Initial consultation to determine if patient is suitable for prosthetic treatment ➢ Record of case history ➢ Determine method of retention (implant, mechanical: e.g. spectacle, adhesive retained)
IMPRESSION TAKING	➢ Impression taking of defect and surrounding tissue as well as of reference anatomic structures (e.g. opposite ear)
MODELLING OF PROSTHESIS	➢ Fabrication of master model ➢ Modelling of facial prosthesis in wax ➢ Trial fitting of wax pattern and alterations as required
PREPARATION OF DENTAL STONE MOULD	➢ Design and fit of wax pattern is approved, wax pattern is invested in dental stone mould ➢ Once stone has set, wax is removed and mould prepared for packing with silicone elastomer
COLOUR MATCHING ELASTOMER TO NATURAL SKIN	➢ Silicone elastomer is custom coloured to match patient's skin tone ➢ Colour matching performed using a) Traditional trial and error method b) Computerised colour formulation ➢ Colour match is completed, elastomer is packed into prepared stone mould and cured
FITTING OF PROSTHESIS	➢ Prosthesis is divested and trimmed ➢ Fit of prosthesis is checked and approved ➢ Application of extrinsic tinting if required

.

Table 1.1: Traditional method of manufacturing maxillofacial prostheses; working sequence.

1.4. Statement of problem

1.4.1. Degradation of colour and mechanical properties of maxillofacial elastomers

Unfortunately, observed colour changes of maxillofacial prostheses in clinical service are very common and one of the main reasons for their frequent renewal (Andres *et al*. 1992; Gary *et al*. 2001; Haug *et al*. 1999; Polyzois 1999). A discoloured orbital prosthesis (Fig. 1.1) has degraded in colour within a period of one year. Furthermore, its fine feathered edges have curled away and worsened the overall appearance of this facial prosthesis. This presented patient case demonstrates the degree of colour changes frequently observed in clinical practice.

(a) (b)

Fig. 1.1: (a) Discoloured and ill-fitting orbital prosthesis in situ, (b) close-up.

Many maxillofacial silicone elastomers and colourants are available today for the manufacture of facial prostheses but their performance in terms of colour stability is still far from ideal. However, the colour degradation of maxillofacial prostheses has been described as a complex phenomenon and is comprised of several contributing factors: environmental factors (UV-light, humidity, air pollutants),

personal habits of patients, the colour stability of silicone elastomer and colourants, as well as the loss of extrinsic colouration. Nevertheless, UV-light has been identified as one of the key factors contributing to the colour changes of maxillofacial appliances (Han *et al*. 2010; Lemon *et al.* 1995; Tran *et al*. 2004).

1.4.2. Colour differences between maxillofacial prostheses and skin as a result of colour matching

Mc Kinstry (1995) found that patient satisfaction with extra-oral prostheses declined within the first three years of service. This phenomenon may be attributable to the fact that from the perspective of the patient, difference in colour is one of the most important parameters when evaluating the performance of extra-oral facial appliances (Chen *et al.* 1981; Jani and Schaaf 1978).

A good colour match between natural skin and maxillofacial prostheses at the time of fitting is vital for successful rehabilitation. This colour matching process involves the traditional trial and error approach, where different pigments at varying amounts are gradually added in stages to the base elastomer until a good colour match with the skin that surrounds the defect has been achieved. However, the success of this method relies upon the expertise of the clinician.

Therefore, attempts have been made to transform the colour matching process into a repeatable, predictable and reliable method. Today, computerised colour formulation has become commercially available in order to colour match silicone elastomer with natural skin. When fabricating a new orbital prosthesis for the patient shown in Fig. 1.1, the base skin colour was established using colour formulation software. Using this base colour, further individual skin colours were mixed in order to replicate the colouration of various skin areas such as the upper and lower eye lid, the area of the inner canthus as well as freckles and shaded skin areas. Figs. 1.2 (a) and (b) show the new orbital prosthesis in-situ demonstrating a good colour match and fitting between elastomer and natural skin.

(a) (b)

Fig. 1.2: New orbital prosthesis in situ demonstrating good colour match and fitting, (a) without and (b) with glasses

However, the approach of utilising colour formulation software for fabrication of facial prostheses still represents an early stage and has not yet been generally accepted by all clinicians; furthermore, the commercially available computerised colour formulation systems require detailed assessment in order to facilitate their application in daily clinical use.

1.5. Ideal properties of maxillofacial materials

Ideal properties of a maxillofacial material have been described by various authors (Lewis and Castleberry 1980; Lontz 1990; Moore *et al*. 1977; Schaaf 1975) and are summarised below (Table 1.2).

NON IRRITANT	The material should not irritate the tissues with which it comes into contact.
PLYABILITY	It should have similar physical and mechanical properties as natural human skin. Therefore, it should be soft, pliable and adaptable to facial movements.
DENSITY	The material should be of light weight in order to prevent detachment during wearing.
COLOUR	It should be easy to colour and colour match the material to natural skin tones, the material perfectly blending with surrounding living tissues.
HYGIENE	The material must be hygienic, non-porous and withstand daily cleaning and disinfection without deterioration.
DURABILITY	It must not be affected by environmental impacts such as sunlight, humidity and personal patient habits such as smoking and personal prosthesis cleaning regimens.
THERMAL CONDUCTIVITY	The prosthetic material should be a poor conductor of heat.
MANIPULATION	It should be easily manipulated, and should not require any extensive equipment and complicated working techniques.

Table 1.2: Ideal properties of maxillofacial materials.

However, a general conclusion drawn from the literature states that success of maxillofacial prostheses is still limited by the mechanical and physical properties of the materials used for their fabrication and that the most ideal materials are still to be developed.

1.6. Evolution in the art of maxillofacial prosthetics

It is impossible to determine at what time in history maxillofacial prosthetics was first introduced. However, various authors who have investigated the history of facial prosthetics agreed on first evidence of facial prosthetic devices during the fourth Egyptian dynasty around 2500 B.C. (Conroy 1983; Conroy and Hulterstrom 1978; Over 1989; Popp 1939). Since then, the materials and manufacturing processes in the fabrication of facial appliances have changed; important milestones and previously used materials for manufacturing of maxillofacial prostheses are summarised below (Tables 1.3 and 1.4).

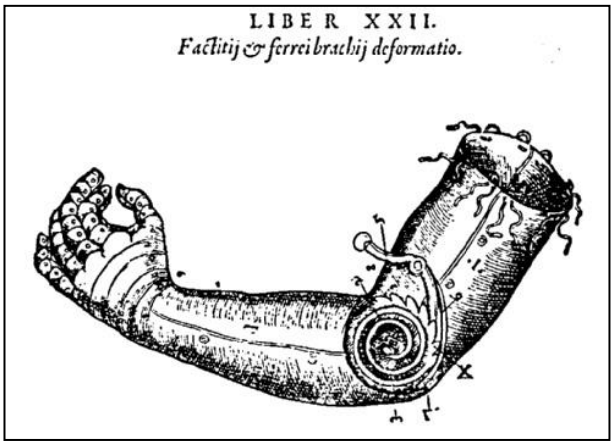
Time period		Achievements / previously used materials	References
16th century	1579	Paré (French surgeon) published "The Opera" in which he describes and shows examples of limb and facial prostheses (Fig: 1.3 a, b) Brahe (1546-1601), a famous astronomer of his time, wore a nasal prosthesis made from metal and painted with oil colours to match his skin to cover his nasal defect (Fig: 1.4)	Conroy 1983 and 93; Lee 1972; Ring 1991
18th century	1728	Fauchard published his book "Le Chirurgien Dentiste" which is considered a landmark and milestone in the treatment of maxillofacial defects	Bulbulian 1965; Conroy 1993; Ring 1991
19th century	1820	Delabarre, a French surgeon and dentist published a book on mechanical dentistry where he introduced innovations in maxillofacial prosthetics	Conroy 1983; Over 1989; Roberts 1966; Van Doorne 1994
	1832	Whymper describes the fabrication of a facial appliance from the original plaster cast of the face to the cast silver mask, known as "The gunner with the silver mask" (Fig: 1.5 a, b)	
	1870	Norwegian Georg Moe fabricated and reported about the production of a hard rubber (vulcanite) facial prosthesis	

Table 1.3: Milestones and previously used materials; until the end of 19th century.

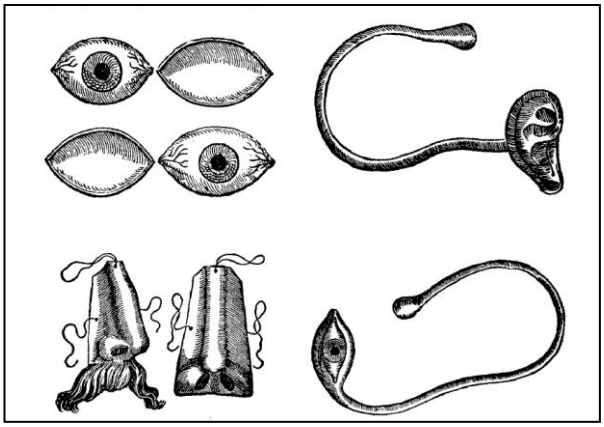
Time period		Achievements / previously used materials	References
20th century	1916	In Germany, Klocke introduced technique of fabricating prostheses made from gelatine	Conroy 1983; Trester 1983
	1920s	Kazanjian used vulcanite in combination with various metals and revived the concepts of maxillofacial prosthetics Latex (natural rubber), pigmented latex was poured through opening into dental stone mould and then heat polymerised; physical and mechanical properties were weak; rapid material deterioration; was difficult to colour match latex to natural skin	Bartlett 1975
	Since World War II	Polymethylmethacrylate, PMMA; manufacture of intra-oral and extra-oral prostheses; ease of use but hard material; flexible material produced by adding plasticiser but resulted in poor physical and mechanical properties and its leaching caused skin irritations	Bartlett 1975; Chalian and Philips 1974; Craig *et al*. 1980
	1940s	Introduction of PVC; was for several years most frequently used; addition of plasticiser required; complex manufacturing process; two main drawbacks: leaching of plasticiser and resultant material hardening, yellowing due to effects of UV light	CDMC 1975; Craig *et al.* 1980; Craig 1985
		Polyurethanes; produced prostheses with life like appearance, flexibility, good tear strength; manufacturing process was technique sensitive and outside handling capability of maxillofacial laboratories	Bartlett 1975; Craig *et al.* 1980; Yu *et al.* 1980

Table 1.4: Milestones and previously used materials, from begin of 20th century.

As demonstrated above, many materials have been used in the construction of maxillofacial prostheses; however, most of them have been discarded as a result of their limited suitability for facial applications.



(a)



(b)

Fig. 1.3: (a) Example of arm prosthesis, and (b) facial prostheses designed by Paré.

(Conroy, B.F. 1983)

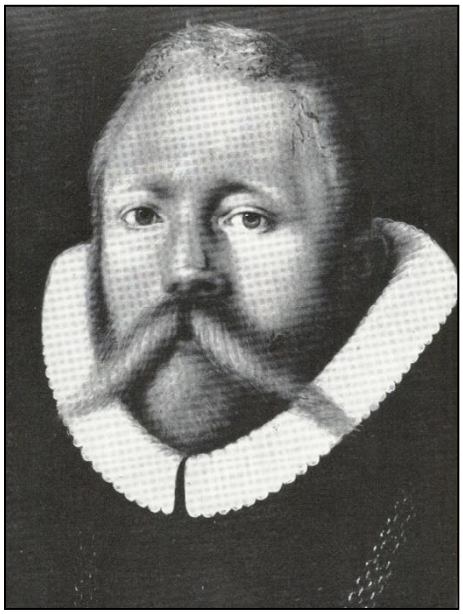
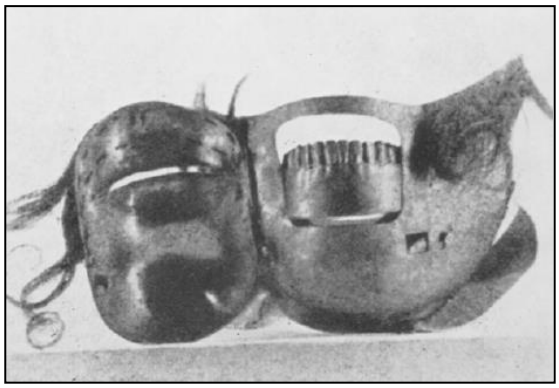


Fig. 1.4: Tycho Brahe

(Lee, D.C. 1972)



(a) (b)

Fig. 1.5: The gunner with the silver mask, (a) and (b).

(Roberts, A.C. 1966)

1.7. Silicones

Silicone elastomers are polymers that differ from most other polymers in that their basic chemistry consists of alternating oxygen and silicon atoms instead of carbon atoms. In the 1940s, J.F. Hyde of Corning Glass developed a technique for synthesis of modern commercial silicone elastomers, polydimethylsiloxanes (PDMS); and in the 1950s, Holter constructed a hydrocephalus shunt from PDMS and demonstrated that silicone rubber could facilitate itself as a biomaterial and aid the treatment of many health conditions (CDMD 1975; Colas and Curtis 2004; Hulland 1979).

Silicone elastomers demonstrate good mechanical and physical properties, excellent biocompatibility and bio-durability as well as good processing properties; and these characteristics make it a favourable biomedical material that can be used for various medical applications involving intimate contact with human tissues and bodily fluids (CDMD 1975; Colas and Curtis 2004;Hulland 1979).

Today, silicone elastomer has become the most frequently used material for fabrication of maxillofacial prostheses which is related to its durability, good physical and mechanical properties, its ability to be easily coloured and colour matched with natural skin (Lewis and Castleberry 1980; Lontz 1990; Thomas 2006).

1.7.1. Silicone elastomer types

The polymerisation of PDMS is achieved by chemical linking of the polymer chains, while incorporation of silica fillers improves the physical and mechanical properties of the material. Polymerisation can be achieved by addition or condensation cross linking reactions; they can be cured at room temperature and are therefore known as room temperature curing (RTV) silicones. Polymerisation is also possible at elevated temperatures (approximately 85°C to 100°C); these

elastomers are known as high temperature curing (HTV) elastomers (Colas and Curtis 2004; Lynch 1978; Raymond 1977).

1.7.1.1. Addition polymerisation

Addition cured silicone elastomers are commonly referred to as platinum catalysed silicones and are generally two-part systems with each part containing different functional components. Generally, the Part A component contains vinyl functional silicones and the platinum catalyst, whereas Part B contains vinyl functional polymer and hydrogen-functional cross-linker. The cure chemistry involves the direct addition of hydrogen-functional cross-linker to the vinyl functional polymer, forming an ethylene bridge crosslink. The polymerisation of addition cured silicone elastomers can be accelerated at higher temperatures if a heat activated platinum catalyst is used (Lynch 1978; Raymond 1977; Thomas 2006).

1.7.1.2. Condensation polymerisation

Condensation acetoxy systems are typically used in the formulation of one-part dispersions; they are most frequently used as sealants and adhesives in maxillofacial prosthetics. These materials are very effective when cured in thin sections and provide good adhesion to most substrates. The cure system consists of hydroxyl-terminated polymers, alkyltriacetoxysilane cross-linkers and a tin catalyst. This one component product cures when exposed to ambient humidity at room temperature. Acetic acid is liberated during the polymerisation process and evidenced by a vinegar-like odour that disappears when full cure is achieved (Lynch 1978; Thomas 2006; Winter 1979).

1.7.1.3. Silicones in maxillofacial prosthetics

Barnhart and Robinson (1958) were the first to use Silastic 501 silicone rubber (Dow Corning) within the field of maxillofacial prosthetic rehabilitation. It possessed favourable material properties as it was a flexible and dimensionally

stable material. It was further possible to mix colourants into Silastic 501, which is known as intrinsic colouration, and it could be processed by using dental laboratory techniques and equipment.

However, in 1960, the Dow Corning Company of America introduced a new silicone rubber material that superseded all previously used materials within the field of maxillofacial prosthetics. This material demonstrated flexibility and good physical and mechanical properties including tear strength, tensile strength and hardness over a wide temperature range. This silicone rubber material contained PDMS as the base polymer, cross-linking chemicals and was reinforced with silica fillers in order to improve the materials' physical and mechanical properties (Raymond 1977).

Today, a wide range of silicones are available for use within the field of maxillofacial prosthetics and liquid platinum curing silicone elastomers (LSR) have become the most frequently used materials. They are available as either RTV or HTV materials offering a range of specific characteristics including working time, hardness and physical and mechanical properties.

Condensation curing silicones are usually RTV elastomers. They do not require heat for the polymerisation process but moisture and air. Most condensation curing silicones in maxillofacial prosthetics are one part systems and of high viscosity and paste like consistency. They are usually used as sealants in order to cover and protect extrinsic facial prosthesis colouring (individual surface tints) and used as adhesives in order to bond silicone elastomers to one another as well as to some synthetics and metals.

Another type of addition platinum curing elastomers involves higher density or consistency silicones (HCR) which demonstrate enhanced physical properties over LSR silicones as a result of longer polymeric chains coupled with higher filler loading. These high density silicones need to be processed using a two roll mill where mixing of silicone components (base elastomer and cross-linker) and incorporation of pigments is achieved by feeding the elastomer / pigment mix

through the mill before being sculpted into shape ; however, they are more frequently used in body and limb prosthetics (Thomas 2006).

1.7.2. Physical and mechanical properties of silicone elastomers

Tear strength, tensile strength and hardness have been identified as important mechanical properties a silicone elastomer should possess to be suitable for maxillofacial use.

Tear strength of a maxillofacial silicone elastomer is a very important property as the feathered edge of a facial prosthesis is in particular susceptible to tearing due to the uptake of skin lipids and the handling pattern of patients (Goldberg *et al.* 1980; Winter 1979). Tensile strength and elongation of silicone are regarded as an indication of overall strength of the elastomer providing information on the materials' ability to deform under mechanical stress. High tensile strength and elongation are desired especially when the feathered edges of the prosthesis are peeled away from the facial tissue. Hardness is another important property of maxillofacial silicone elastomers as a facial prosthesis should possess characteristics close to those of natural skin (Aziz *et al*. 2003; Bellamy *et al*. 2003; Brown 1986; Raymond 1977).

1.7.3. Ideal values of physical and mechanical properties

Sweeney *et al.* (1972) were the first to publish, and Conroy *et al.* (1979) and Lewis and Castleberry (1980) later updated data describing desired values for physical and mechanical properties of a maxillofacial elastomeric material. A summary of desired values for tear strength, tensile strength, elongation and hardness of maxillofacial silicones is provided in Table 1.5.

Year of publication	Authors	Desired values of physical and mechanical properties			
		Tear strength	Tensile strength	Modulus of elasticity / Elongation	Hardness (Shore A)
1972	Sweeney *et al.*	33 ppi	1800 psi	600 psi	48-52
1979	Conroy *et al.*	Minimum in excess of 10 kNm^{-1} Optimum in excess of 40 kNm^{-1}	Minimum in excess of 5 MNm^{-2} Optimum 10 MNm^{-2}	Minimum in excess of 500 % Optimum between 500 to 1000 %	Minimum 25 to 30 Optimum 25 to 55
1980	Lewis and Castleberry	30 to 100 ppi	1000 to 2000 psi	5 0 to 250 psi	25 to 35

Table 1.5: Ideal values of physical and mechanical properties of facial elastomers. (pounds per inch = ppi; pounds per square inch = psi)

Lewis and Castleberry (1980) showed in their study that chemical structural differences of commonly used elastomers at that time resulted in variations of physical and mechanical properties tested. As a consequence, more studies were carried out on available silicone elastomers and the development of new elastomers to achieve a favourable combination of high tear strength, tensile strength and elongation at break alongside with low hardness which represent desired characteristics for facial prostheses (Hatamleh *et al.* 2016).

1.8. The use of pigments in maxillofacial prosthetics

Silicone elastomers are most frequently used in the manufacturing process of maxillofacial prostheses and are for this particular application coloured with a variety of pigments in order to establish a good colour match between elastomer and natural skin. A range of colourants are available to the clinician and include pigments of organic and inorganic origin as well as fibre flocking to create a natural and authentic appearance of skin coloured silicone elastomer.

1.8.1. Organic pigments

Natural organic pigments were derived from vegetable, animal or insect sources but demonstrated great likelihood to fade and examples include madder, indigo, gamboge. Today, almost all have been replaced by synthetic organic pigments which are carbon based molecules manufactured from petroleum compounds, acids and other chemicals. Alizarin, azo-pigments (yellow, orange and red colours), phthalocyanine (blue and green colour range) and quinacridone (a lightfast red-violet pigment) belong to the group of synthetic organic pigments. These pigments are often the most saturated and strongest tinting colourants; however, they can be expensive to manufacture and exhibit a high degree of light fastness which describes the ability of a pigment to withstand exposure to light (Mc Laren 1986).

1.8.2. Inorganic pigments

Inorganic pigments are classified as naturally occurring pigments derived from materials such as earth and metals and include ochres, umbers and siennas. These have been used as colourants since prehistoric times and represent very stable colours. Pigments with the same names are also produced synthetically. Further examples of synthetic inorganic pigments are cadmium yellow / orange / red, cobalt blue and titanium white. Synthetic inorganic pigments generally demonstrate excellent colour consistency. They are cheaper to buy and available in larger quantities than natural inorganic pigments. However, inorganic pigments

are generally less vibrant; their colour palette for maxillofacial applications in particular is therefore more limited when establishing natural skin tones (Mc Laren 1986).

1.8.3. Fibre flocking

Microfibre flocking is used to impart colour and depth to maxillofacial elastomer. It is available in different colours including reds, purples, white and a range of beige / skin coloured tones. There is hardly any information on the application of fibre flocking. Thomas (1994 and 2006) stated that adding pigments to elastomer results in a rather 'flat'appearance of silicone as a result of the absorption and scattering characteristics of pigments. Therefore, fibre flocking is added as this, apart from imparting colour, creates a material 'depth' due to its light scattering characteristics. Fine (1978) reported that the multiple refractions, transmissions and reflections between and within fibre flocks result in the optical effect of three-dimensional appearance of elastomer and thereby simulate the variegated translucency of natural skin.

1.9. Colouring maxillofacial silicone elastomer

1.9.1. Intrinsic colouring

The two general methods for colouring maxillofacial elastomer involve intrinsic and extrinsic colouring. Intrinsic colouring describes the incorporation of internal colour within the silicone elastomer. This technique permits a layering of different colours which in turn lends depth to colour and thereby creates a natural appearance of the silicone elastomer and consequently of the facial prosthesis (Thomas 1994 and 2006).

1.9.2. Extrinsic colouring

If intrinsic colouring has been performed correctly, only minimal extrinsic colouring or staining should be required. However, this is the process that brings

a facial prosthesis ‘to life’ by adding surface details such as freckles, veins, hair or natural areas of shadow. This procedure involves application of pigments and flocking to the surface of the silicone. For extrinsic tinting, pigments are diluted in a carrier substance and carefully applied using a paint brush. Once extrinsic colouring has been completed it is sealed with a commercial sealant (Thomas 1994 and 2006). One part acetoxy silicone elastomers are generally used for extrinsic sealing of facial prostheses and today, a variety of sealants is available to the clinician. Frequently used products include the A-564 Extrinsic Sealant Kit from Factor II Inc. (Lakeside, Ariz.) or P-799 Extrinsic Sealant from Technovent Ltd. (Bridgend, UK), the latter been used in this study.

1.9.3. Base skin shade

The underlying skin colour of a patient which does not account for any vascular or cartilage tissue colour, or any other individual skin colour shade (freckles or skin imperfections) has been defined as a patient’s base skin shade. Thomas (2006) described that a base shade can be established by observing the tissue under pressure and that with removing the vascular appearance of skin the underlying lighter base shade can be illustrated. Based on this technique, individual pigments are then added to the elastomer (intrinsic colouring) to establish the skin base shade colour; subtle fibre flocking is incorporated as the last step to replicate vascularity of skin.

1.9.4. Individual skin shades

Once mixing of the base shade has been completed, it is necessary to establish various individual skin shades for specific local skin areas. Such areas may for example include the upper and lower eyelid, inner canthus of the eye, shade areas below the lower eye lid or adjacent to the nostrils, the helical rim of the ear or the distal tip of the finger. These colours are established in the same manner as the base shade utilising the intrinsic colouring method, adding pigments and fibre flocking. However, they are usually slightly stronger in colour as they will be applied first inside the mould as a thin surface layer and blended with the base

shade colour. Therefore, some of the colour will be naturally absorbed by this silicone layering process (Thomas 2006).

1.9.5. Established colouring techniques in maxillofacial prosthetics

Variations of the two general methods of prosthesis colouring have been established and described in the literature; they are summarised in Table1.6.

Year of publishing	Authors	Colouring techniques
1941	Bulbulian	➢ Mixed water colour into latex
1943	Clarke	➢ Used dry pigments and dyes to colour latex
1960	Barnhart	➢ Used pigmented methyl-methacrylate for intrinsic colouring of silicone rubber
1967	Tashma	➢ Used ground acrylic resin and dye concentrate to colour base elastomer
1969	Firtell and Bartlett	➢ Eliminated use of acrylic resin due to adverse effects on mechanical properties of elastomer ➢ used pure earth pigments to produce stock colours of various hues for intrinsic colouring ➢ extrinsic tinting by using a brush on technique and emphasised on problem of delamination of extrinsic sealant layer
1969	Oulette	➢ introduced airbrush method for extrinsic tinting
1970	Schaaf	➢ described method in which artist oil colours were deposited beneath silicone surface of prosthesis using a tattooing device but caused weakening of elastomer due to perforations
1971	Bartlett *et al.*	➢ introduced use of silicone medical adhesive as sealant layer instead of ordinary silicone rubber and stated improved adherence due to chemical bonding
1978	Fine *et al.*	➢ used silicone medical adhesive and coloured flocking rather than pigments for extrinsic tinting as flock fibres provided a three-dimensional, natural appearance
1983	Hanson *et al.*	➢ utilised premixed mineral earth pigments used in commercially available foundation cosmetics for intrinsic and extrinsic colouring

Table 1.6: Variations of maxillofacial elastomer colouring techniques.

1.10. Colour perception in maxillofacial prosthetic rehabilitation

Nimeroff (1968) quoted the Committee on Colorimetry of the Optical Society of America with regards to the definition of colour which states that:

'Colour consists of the characteristics of light other than spatial and temporal inhomogeneities; light being that aspect of radiant energy of which a human observer is aware through the visual sensations which arise from the stimulation of the retina of the eye'.

To simplify this statement, colour results from the interaction of an object, a light source, and the visual capacity of an observer and is demonstrated in Fig. 1.6. These events are closely interrelated and any change can result in a change in the perceived colour (Babbage 1977; Sproull 1973).

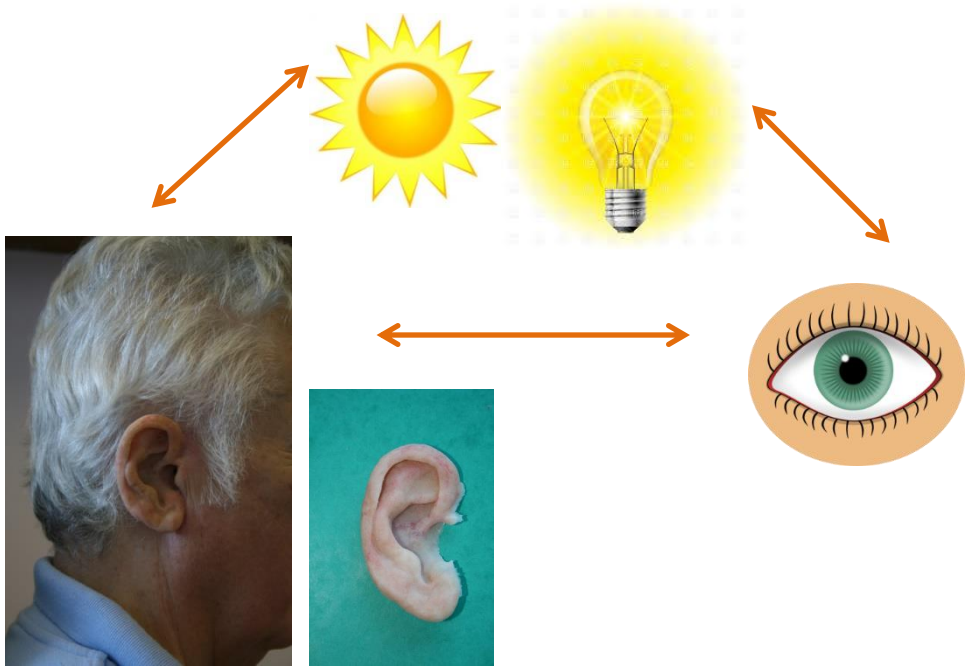


Fig. 1.6: Colour as a result of interaction of a light source, an object and the visual system.

1.10.1. Metamerism

Berns (2000) described that when two illuminated objects produce the same cone signal response in our visual system, the two considered objects will be perceived as being the same colour.

Metamerism is defined as the phenomenon wherein two colours having different spectral compositions match one another (Hunt and Pointer 2011). However, the fact that illuminated objects do not have to have identical spectral properties in order to match in colour makes it possible to reproduce colours without using identical materials. In maxillofacial clinical practice, it is important to understand that without metamerism a facial prosthesis could never match a patient's skin colour. Nethertheless, metamerism also involves the effect of two coloured samples matching in one situation but not in another (Berns 2000; Hunt and Pointer 2011).

1.10.2. The influence of light on colour perception

A physical stimulus in form of light is required to produce colour of an object and this greatly affects the appearance of that object. In maxillofacial prosthetics, the principles of varying light sources need to be considered as they directly affect the colour match between skin coloured elastomer and the natural surrounding skin (Johnston 2009; Paravina *et al*. 2009). This means in clinical practice that the type and level of illumination should be the same to that under which the prosthesis will be viewed in clinical service.

It is a common misconception that a colour match performed under one selected single light source will match under all other light sources; in fact, it will produce a colour match that is conditional to that particular light source and will not reduce metamerism. Each light source can be described by measuring its relative power at each wavelength of the visible spectrum and by its colour temperature; and the amount of relative power at a specific wavelength as well as colour temperature will either enhance or reduce the mismatch between the spectral

reflectance of the target skin colour and coloured silicone. Our visual system is more or less sensitive to different areas of the visible spectrum if the relative power of one light source is different from another which enables an obsever to detect this spectral mismatch (Berns 2000).

1.10.2.1. Illuminant metamerism

Illuminant metamerism describes the effect of two objects looking the same colour under one illuminant but looking a different colour when viewed under another illuminant (Berns 2000; Hunt and Pointer 2011). This may be experienced in maxillofacial clinical practice as a good colour match between the facial prosthesis and a patient's skin colour when viewed in the clinic room under fluorescent light, but representing a colour mismatch when viewed under natural light outside.

To minimise the effect of illuminant metamerism, it is essential to have a set of standardised light sources under which the colour match is assessed. It is recommended to use different light sources (daylight simulators, fluorescent lighting, LED lighting) when colour matching elastomer with natural skin and advised to ask patients which light source is most important to them and where they are most conscious of being noticed.

1.10.3. Influence of observer on colour perception

1.10.3.1. Human colour vision

Human vision and colour vision is a very complex process that involves the nearly simultaneous interaction of both eyes and the brain through a network of neurons, receptors and other specialised cells. This process can be described in a simplified way as light that is entering our eyes is imaged onto the retina which is located at the back of the eyeball. Light receptors absorb there a portion of the incident light and generate a signal that is eventually interpreted by the brain. The

main physiological structures involved in human vision are illustrated in Fig. 1.7.

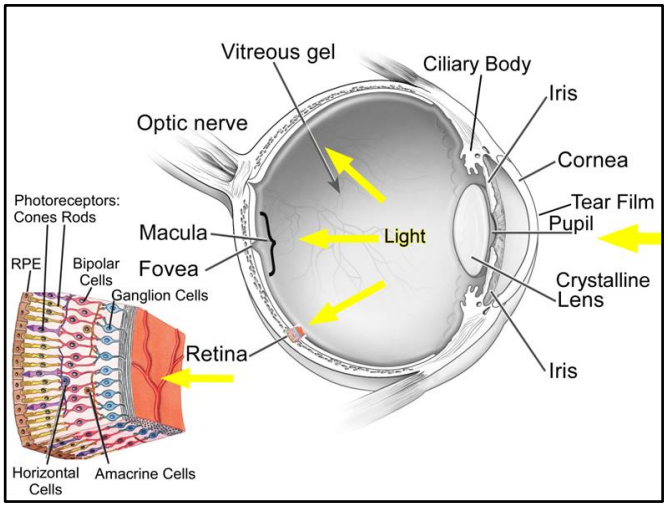


Fig. 1.7: Detailed anatomy of the human eye.
(Vera-Díaz and Doble 2012)

The quality of the retinal image depends on various factors including absorption, scattering and focussing properties of the cornea, lens and fluids that fill the internal eyeball (Berns 2000; Fairchild 2013).

However, the chemical compounds that form colour receptors as well as their physical shapes vary among the population and within the retina. Furthermore, the amount of macular pigments as well as the absorption and scattering properties of the ocular lens are different from one person to another. As a result, colour vision among observers with a normal colour vision varies significantly (Berns 2000; Fairchild 2013).

There are two types of photo receptor cells that are responsible for colour vision; rod cells which enable for night vision, and cone cells which are responsible for high acuity tasks like reading as well as for human colour vision. Cone cells can be subcategorised into three types and are referred to as L, M and S which represents their sensitivities to long (L), middle (M) and short (S) light wavelength regions. Incident light produces cone signals which integrate the light

at all wavelengths and thereby reduce the entire spectrum of incident light to three signals, one for each cone type and this is called trichromacy (Berns 2000; Fairchild 2013).

1.10.3.2. Observer metamerism

As it has been highlighted in the section above, there is a significant range of colour vision amongst different people who are all considered to have normal colour vision. Observer metamerism is based on this fact and described as the situation where two colour samples match for one person but fail to match when seen by a second person, and is the result of their different light receptor sensitivities (Berns 2000). This may become problematic when these two persons are, for example, the clinician and the patient.

1.10.3.3. Colour vision deficiency and colour blindness

Change in colour vision occurs with increasing age and a commonly observed change is related to yellowing of the lens as a result of UV-light exposure; its extended appearance is known as a cataract. However, change in colour vision can also be acquired and may be related to chronic illnesses such as diabetes mellitus, glaucoma, macular degeneration or retinitis pigmentosa. Other possible reasons may be accidents, the use of medication, industrial or environmental chemicals (Fairchild 2013).

However, genetic colour deficiency affects about 8% of the male and 0.5% of the female population and involves that either one or more colour light receptors are missing. The most common colour deficiency screening test was developed by Isihara (1962) and uses pseudo isochromatic plates which are random dots with embedded numbers; an example is shown in Fig. 1.8. An observer with deficient colour vision, missing either L or M cones, would only see the random dots and not recognise the embedded numbers. Colour deficiency screening is mandatory for anyone carrying out critical colour judgements (Berns 2000; Hunt and Pointer 2011).

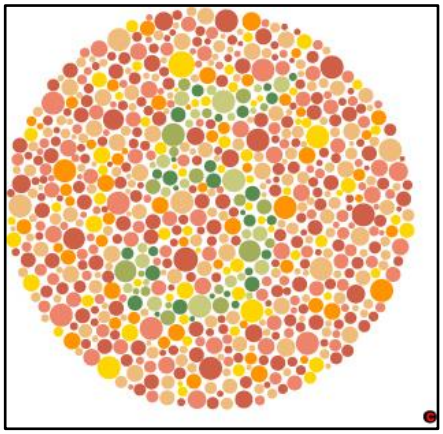


Fig. 1.8: Pseudo isochromatic plate of the Isihara colour deficiency test. (From: https://websites.godaddy.com/blob/aa59a632-c7cb-48a4-b57e-fc2dd8327679/downloads/1bhgci3i5_342415.pdf?36b73963)

1.10.4. Influence of objects on colour perception

1.10.4.1. Human skin

Generally, the physical processes of light transmission, reflection, absorption and scattering take place when incident light strikes natural skin. Skin can be divided into three main layers including stratum corneum, epidermis and dermis; and the optical properties of these layers play an important role whenever skin is involved as the site of photobiologic reactions. Only a small amount of incident light is refelected on the surface of skin and the remaining 93% to 96% of light are transmitted, absorbed or scattered within the different layers of skin; the collagen fibres of the dermis in particular are the principal scatterers of light (Anderson and Parrish 1981; Andreassi and Flori 1995; Kollias 1995).
Chromophores are light absorbing molecules and located within the different layers of skin; they include melanin, carotenoids, hemoglobin and oxyhemoglobin. Melanin, confined to the stratum corneum and epidermis, is essentially the pigment imparting colour to human skin. Its colour ranges from slight yellowish to dark black, giving rise to a wide range of discernable skin

shades and is reflected in the presence of various ethnic skin types (Anderson and Parrish 1981; Andreassi and Flori 1995; Kollias 1995).

The dominant chromophore in the dermal layer of skin is and exists as either oxyhemoglobin or reduced hemoglobin. Oxyhemoglobin is located in blood capillaries and arterioles and imparts a bright red colour to these structures, whereas reduced hemoglobin is found in venules and is responsible for their bluish colour. Carotenoids are acquired yellow pigments but have little influence on the colour of skin except from excessive accumulation (Anderson and Parrish 1981; Andreassi and Flori 1995; Kollias 1995).

1.10.4.2. Silicone elastomer

In order to produce a life-like appearance of facial prostheses, approximation of optical properties of skin and skin coloured silicone elastomer is required and is achieved when both exhibit similar responses to incident light. Maxillofacial silicone elastomer is a translucent material; and to mimick a skin like appearance in silicone, pigments and fibre flocking are added to the material and both impart colour through absorption of light at specific wavelengths.

In maxillofacial applications, surface texture has a profound impact on the appearance of coloured silicone elastomer; whilst uncured silicone is highly glossy, the final processed silicone prosthesis has a matt finish and is more similar to natural skin. In clinical practice, surface gloss of elastomer is minimised as a result of the manufacturing process of facial prostheses when processing the silicone in a dental gypsum mould (Thomas 2006).

1.10.4.3. Translucency and opacity of maxillofacial elastomer

Thomas (2006) described natural skin as predominantly opaque with translucent quality at the surface and highlights that only a balance of these characteristics results in a life-like appearance of maxillofacial elastomer. He further stated that a too translucent coloured silicone will look ‘grey’ and ‘watery’, and that this

colour match will be incorrect even if the correct shades of colour have been utilised.

Clarke (1943) already recognised that excessive application of opaque pigments would destroy the translucency of the final prosthesis when discussing intrinsic colouring of latex with pigments and dyes. Aina *et al.* (1978) used synthetic inorganic iron oxides and titanium dioxide at 1% and 0.1% by weight when colour matching elastomer to African skin tones and found that 1% weight of the black pigment completely masked the other used pigments. This was only overcome by reducing the black pigment to 0.1% weight, or by applying a smaller portion of the 1% black stock colour. It was shown that a careful selection of pigment concentration is required to achieve a translucency and opacity level that approximates those of natural skin.

Further studies were performed to determine the appropriate pigment concentration needed to produce a skin like appearance of elastomer (Table 1.7).

Year of publication	Author(s)	Recommended pigment weight concentration (%)
1995	Johnston *et al.*	Dry pigments 0.10 Fibre flocking 0.20
1995	Erb	Caucasian skin type 0.15 African skin type 0.30
1996	Troppmann *et al.*	Caucasian skin type 0.15 – 0.25
2000	Seelaus and Troppmann	Caucasian skin type 0.16
2008	Coward *et al.*	African-Canadian skin type 0.20 – 1.96

Table 1.7: Recommended pigment concentration (%) for optimum translucency/opacity of maxillofacial elastomer.

1.10.5. Perceptability and acceptability thresholds of colour differences

The big challenge clinicians face in prosthetic rehabilitation is to find a good balance when colour matching facial prostheses with the surrounding skin. A successful colour matching result would be achieved when the 'colour static' prosthesis blends at all times with the always changing, 'dynamic' colour of skin. One of the main questions is, when does and when doesn't a prosthesis and its surrounding skin match in colour? What minimum difference in colour can be perceived by the human eye? And what colour difference would be or would not be acceptable by the observer?

The use of colour is versatile and so are the problems concerned with colour differences. Kuehni and Marcus (1979) stated that established colour difference formulae led to calculated colour differences, expressed as Delta E (ΔE), that correlated only moderately well with the average visually judged colour differences. Since then, the correlation between calculated and visually detectable colour difference has been the focus of research in various fields such as the textile, paint and car industry as well as medicine including dental and maxillofacial applications (Kuehni and Marcus 1979; Leow *et al.* 2006; Lindsey and Wee 2007 and 2010; Paravina *et al.* 2009 and 2015; Ragain and Johnston 2001; Seghi *et al*. 1989).

The aesthetic appearance of facial prostheses is directly related to the success of maxillofacial prosthetic treatment. If a facial prosthesis does not match in colour with the surrounding skin, this difference in colour may be perceived by an observer. Paravina *et al.* (2009) stated that colour difference tolerances can be determined by asking two questions:

'…Can I see a difference in colour…?' for a perceptibility judgement, or
'…Is this difference in colour acceptable…?' for acceptability judgements of colour differences.

It has been stated in dentistry that a nearly perfect colour match corresponds with a colour difference below the 50:50% perceptibility threshold (PT); this means a difference in colour can be detected by 50% of observers. Accordingly, an acceptable colour match represents a difference in colour below the 50:50% acceptability threshold (AT), where the colour difference is described as acceptable by 50% of observers (Lindsey and Wee 2007; Paravina *et al*. 2009 and 2015; Ragain and Johnston 2000).

In 1979, Kuehni and Marcus conducted a study to establish PT and AT for small colour differences in a colour scaling experiment. The authors stated there was no apparent fundamental difference regarding perceptibility and acceptability judgements; however, it was found that a ΔE of 1 was detectable by 50% of observers.

Seghi *et al*. (1989) investigated the relationship between calculated colour difference values and human observer responses involving translucent dental porcelain and found that a ΔE of 1represents a colour difference that is perceivable for the average dental observer group. They further stated that sample pairs producing a measured colour difference value > 2 ΔE were correctly judged by the observer group 100% of the time.

Different values for PT and AT have been reported in paint/textile industry, dentistry (Appendix A) and for maxillofacial applications (Table 1.8).

Year of publication	Author(s)	Skin tone / Ethnic group	PT $\overline{\Delta E}$	AT $\overline{\Delta E}$
2006	Leow *et al.*	Fair skin Dark skin	0.8 1.3	1.80 2.60
2009	Paravina *et al.*	Fair skin Dark skin	1.1 1.6	3.00 4.40
2014	Nacher-Garcia	Overall White Chinese Black Indian	not investigated	1.54 1.61 1.87 2.33 not detectable

Table 1.8: Reported PT and / or AT for maxillofacial applications.

A range of PT and AT has been reported; however, there is no evidence that one of these does represent the most accurate and relevant threshold value. Hence, the intermediate values of 1 ΔE for PT and 2 ΔE for AT, as reported by Kuehni and Marcus (1979) and Seghi *et al.* (1989), were used in this current study when evaluating colour differences. Standardised research methodology and multi-centre investigations are required in order to establish a generally accepted PT and AT for maxillofacial applications.

1.10.6. Visual colour assessment

Facial prosthetic rehabilitation aims to provide a prosthesis that blends well in colour with natural skin and visual assessment of this colour match is generally communicated between at least two persons, the clinician and patient. However, it has been recognised that the visual process of colour evaluation leads to greatly varied and sometimes unpredictable results (Fairchild 2013; Seghi *et al.* 1989).

Generally, the calculated colour differences which are based on instrumental measurements of colour should reflect what observers see; however, Seghi *et al.* (1989) stated that visual colour assessment is the result of physiological and psychological responses to radiant energy stimulation and that this challenges our physiological and psychological rather than scientific skills.

The paper by Kuehni and Marcus (1979) represents one of the key studies on visual assessment of small colour differences and involved ranking of samples in relation to a standard based on perceived colour differences. The authors stated that different observers arranged the samples in a variety of orders; in fact, no sample was ranked the same by all observers.

In 1989, Seghi *et al*. investigated the relationship between calculated colour difference values and human observer responses involving translucent dental porcelain and stated that agreement between perceived and measured colour differences was considerably better than that reported by Kuehni and Marcus (1979).

Paravina *et al.* (2009) performed visual assessment where observers were asked to judge the colour match between skin and silicone and concluded that observers were less sensitive to colour differences in the darker than the fairer colour shades. However, Paravina *et al*. noted two problems involved with visual assessment of colour differences; firstly, that of inconsistency of judgments, where some observers declared imperfect matches for sample pairs with low colour difference values and perfect matches for those with high colour differences. Secondly, some observers also judged all specimens with the same grade. It was reported that these problems were minimised after all observers underwent colour assessment training and were calibrated under the same experimental conditions.

Seelaus *et al.* (2011) performed visual assessment of colour matches between skin and maxillofacial elastomer for African-Canadian subjects. Four silicone samples were fabricated based on corrected colour formulae and achieved as iterative skin colour mixes. A positive correlation was found in judges' assessments of colour matches between sample 1 and 2 of the iterative colour mixes. For these samples, the colour difference between skin and samples decreased with the second iterative mix (sample 2) and this sample was also evaluated a better colour match in comparison to sample 1.

Colour differences further decreased for iterative elastomer and colourant mixes with addition of pigments to the respective skin colour formulae; and for samples 3 and 4, $\overline{\Delta E}$ of 3.5 and 2.17 were achieved, respectively. However, despite decreased calculated colour differences, colour match assessors judged these samples with an increased pigment loading as a 'poorer' colour match. Results of intra- and inter-judge reliability showed that observers were consistent with their scores when judging the same silicone sample a second time but there was variability among judges when assessing the same elastomer sample.

In a study by Bellini (2014), the author carried out visual colour assessments of fabricated silicone samples, with and without flocking and stated that the agreement of judges' scores when assessing the silicone samples against the skin

area was low (38.39%). The author stated that even though the three judges were experts in the field of maxillofacial prosthetics, there were still differences in their experience, visual sensitivity and possibly even their objectivity.

The above studies demonstrate variability of human colour perception and that it is difficult to relate calculated to perceived colour differences of human observers. Paravina *et al.* (2009) reported improved visual colour assessments following colour assessment training and calibration of observers, and Seelaus *et al*. (2011) highlighted the need of sufficient data as well as identification of appropriate persons undertaking colour match assessments in order to obtain more meaningful and conclusive results.

1.11. Colorimetry

Colour is the element that is produced when light, striking an object, is reflected back to the eye. It derives from the spectrum of light (distribution of light power versus wavelength) interacting in the eye with the spectral sensitivities of the light receptors. Colours are familiarly identified with names such as red, yellow, green and blue; however, by defining colour within a three-dimensional colour space, it can be numerically identified.

1.11.1. Attributes of colour

Each colour has its own distinct appearance and can be distinguished from any other colour by using three attributes: hue, chroma and value. Hue describes the colour of an object as it is perceived by an observer such as red, blue, etc.; chroma describes the strength of a colour, how close the colour is to either grey or the pure hue, and value describes the degree of lightness (Berns 2000; Hunt and Pointer 2011). The attributes of colour as a three-dimensional colour system are depicted in Fig. 1.9.

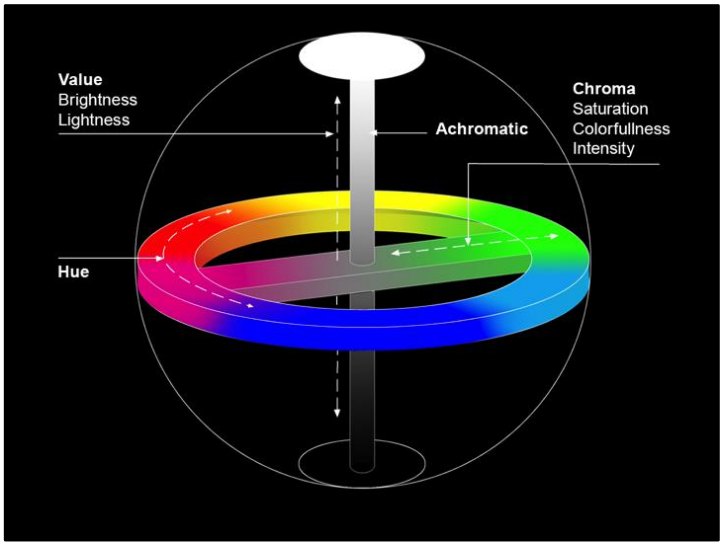


Fig. 1.9: Three-dimensional colour coordinate system using hue, chroma and value.
(From: http://mappingcolor.com/images/jg07rw8df195y7gzc09ooi1ph5490l)

1.11.2. The Munsell scale

Albert Henry Munsell devised one of the most influential colour ordering systems based on the attributes of colour. He illustrated his concept of colour space by painting colour chips which were equally spaced in each of the three dimensions, called the Munsell colour tree (Fig. 1.10). This system is significant from a historical perspective as it is based on human perception and not on a strict set of mathematical values from a light source or illuminant. Moreover, it was devised before instrumentation was available for measuring and specifying colour (Hunt and Pointer 2011; Mc Laren 1986).

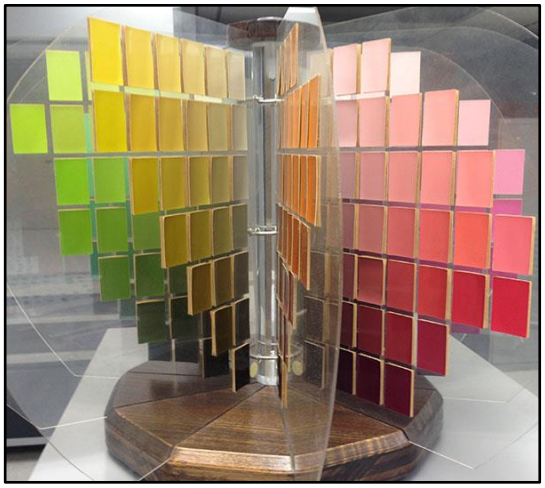


Fig. 1.10: The Munsell colour tree.
(From: http://munsell.com/color-blog/color-tree/)

1.11.3. CIE 1931 standard observer

Founded in 1913, the international commission on Illumination (CIE) has become the professional organisation and international standardisation body concerned with the science and art of light and lighting, colour and vision, and image technology (Schanda 2007).

In 1931, the CIE developed a system for specifying colour by using tristimulus values for three imaginary primaries. This was based on the CIE 1931 observer, and stated that an observer can match a colour stimulus with an additive mixture of the three primaries. The CIE standard observer was derived from experiments where observers were asked to match monochromatic wavelengths of light with mixtures of the three primaries: red, green, blue (RGB). The CIE commissioned this work as the 2°observer but proved being not appropriate for large field visual measurements and therefore, a second set of observer functions was defined in 1964 with a field of 10° (Nimeroff 1968; Schanda 2007).

The tristimulus values, defined as X, Y and Z, correlate with the human colour receptors (cones) and these values may be illustrated graphically by means of a

chromaticity diagram, standardised by the CIE in 1931. Chromaticity coordinates are defined as x, y and z with:

$$\mathbf{x = X/(X+Y+Z)},\ \mathbf{y = Y/(X+Y+Z)},\ \mathbf{z = Z/(X+Y+Z)}\ ;\ \mathbf{x + y + z = 1}.$$

The x and y values constitute the chromaticity of a sample, and if the x and y chromaticity co-ordinates are marked for all spectral colours a horse shoe curved diagram is produced (Fig. 1.11). The original CIE scales are based on tristimulus values; however, the chromaticity coordinates x, y and z are not visually uniform and resulted in the design of a uniform colour space, the CIE L*a*b* from 1976 (Schanda 2007).

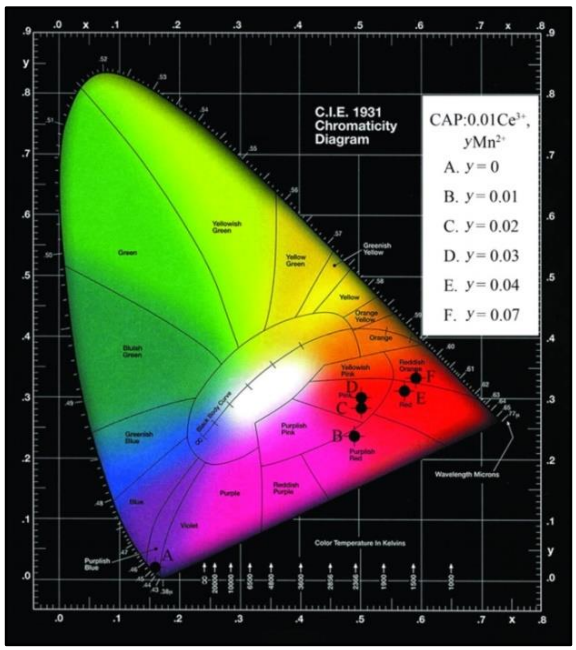


Fig. 1.11: CIE chromaticity diagram.
(From: http://jss.ecsdl.org/content/1/3/R92/F9.expansion.html)

1.11.4. CIE (1976) L*a*b* colour space

The CIE L*a*b* colour scales are based on the opponent-colours theory of colour vision, which says that two colours cannot be both green and red nor blue and yellow at the same time. As a result, single values can be applied to describe the

red/green and the yellow/blue attributes of colour. The L*a*b* colour space diagram identifies the position of a colour in the colour space of visual colours.

The centre axis stands for lightness of colour (L*) with L* = 0 (black or total absorption), L* = 100 (white or total reflection) and the centre of this plane represents neutral or grey. The a* axis represents the red-green shift with positive a* value describing red hues and the negative a* value describing green hues. The b* axis stands for the yellow-blue colour shift and a positive b* value describes yellow hues whereas a negative b* value describes blue hues. With the application of this colour analysis, the amount of light reflected at each wavelength in the visible spectrum (400-700 nm) is measured (Berns 2000; Hunt and Pointer 2011; Schanda 2007).

1.11.5. CIE L*C*h° colour space

The CIE L*C*h° system locates a colour within the three dimensional CIE 1976 colour space based on the L*, C* and h° coordinates. In this method, L* coordinates are the same as in L*a*b*, while the C* and h° coordinates are computed from a* and b* coordinates. The same colour is still in the same location in the colour space but CIE L*a*b* and CIE L*C*h° are two different ways to describe its position.

CIE L*C*h° colour space is three dimensional, with colours located using cylindrical coordinates where L* describes the lightness coordinate (the same as in L*a*b*), C* describes the chroma coordinate, the distance from the lightness axis, and h° defines the hue angle, expressed in degrees. The hue angle starts at the +a* axis with 0°, continuing to 90° for the + b* axis, 180° for - a*, 270° for - b* and back to 360° which equals 0° (Berns 2000; Hunt and Pointer 2011; Schanda 2007).

The principles of L*a*b* and L*C*h° colour spaces are depicted in Fig. 1.12.

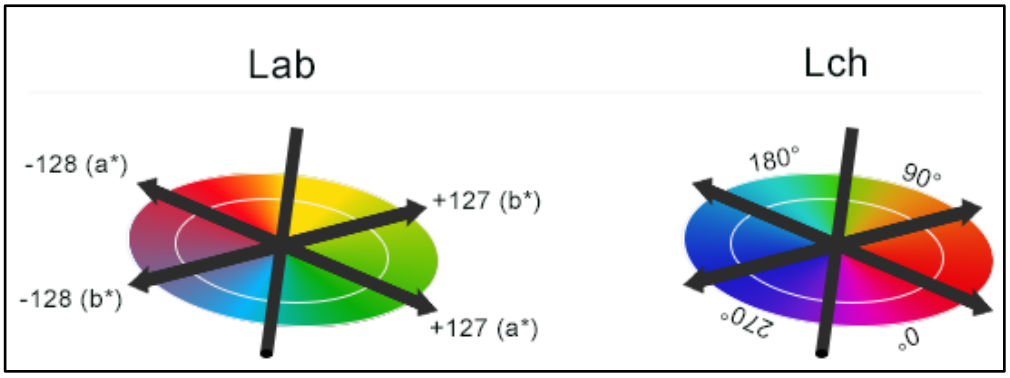


Fig. 1.12: CIE L*a*b* and L*C*h* colour spaces.

(From: http://zschuessler.github.io/DeltaE/learn/)

1.11.6. ΔE CIE L*a*b*

The location of a particular colour within the colour space model allows the calculation of colour difference or distance between two numerically determined colour samples. The colorimetric evaluation of colour differences of surface colours according to the CIE L*a*b* formula is defined by the ASTM D2244. The colour difference (ΔE) between two different colours can be calculated using the equation below (ASTM 1989).

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5};$$

where: $\Delta L^* = L_S^* - L_R^*$, $\Delta a^* = a_S^* - a_R^*$, $\Delta b^* = bs^* - b_R^*$
(R = Reference, baseline reading; S = Sample, actual reading)

The calculation of ΔE represents a numerical value to express the colour difference of two colours, where ΔL* is an indication as to whether a colour has become lighter or darker and Δa* and Δb* values quantify colour changes in the red-green and yellow-blue axes, respectively. However, this colour difference calculation formula does not give an indication of the difference in relation to hue, chroma and lightness.

1.11.7. Successive ΔE calculation formulae, CIE L*C*h°

The original ΔE_{ab} or ΔE 76 colour difference formulae considered a ΔE of 1 to be the smallest difference perceivable by the human eye. This colour differencing equation made it possible to better communicate colour differences under standard illuminants and observers. Nevertheless, it was reported that this formula did not take into consideration that the human eye is more sensitive to small colour differences in some regions of the colour wheel and less sensitive in others. This means that a ΔE of 1could be a small visible difference in one area of the visible spectrum, dark blue colours for example, and a large visible difference in another area, such as light pastel type colours (Berns 2000; Clarke 1984; Habekost 2013).

The CIE revised the original ΔE 76 formula by introducing the ΔE 94 formula in 1994. This formula uses the L*C*h° notation for calculating colour differences and takes certain weighting factors for each lightness, chroma and hue into account. Furthermore, the ability to add a modifier according to the application, either textile or graphic arts, was introduced. The ΔE 94 was further revised and resulted in introduction of the ΔE 2000 (Berns 2000; Habekost 2013).

However, the CIE was not the only body that published a colour differencing equation to address the shortcomings of the ΔE_{ab} formula. In 1984, the Colour Measurement Committee of the Society of Dyers and Colourists of Great Britain (CMC) also developed an equation that is based on the L*C*h° notation of colours. This equation takes the various colour sensitivities of the human visual system into consideration and a ΔE of 1 under CMC gives the same visual difference in all regions of the colour wheel (Habekost 2013).

Investigations showed that conventional ΔE 76 calculations accurately show the difference observers perceive between two colours in about 75% of all cases (Graphic Communications Open Textbook Collective 2015). This original formula has been frequently applied in research involving colour measurement and calculation of colour differences for maxillofacial applications (Al-Harbi *et*

al. 2015; Eleni *et al.* 2008; Hatamleh and Watts 2010[a]; Kiat-Amnuay *et al.* 2009; Mancuso *et al.* 2009; Willett and Beatty 2015); therefore, the CIE L*a*b* and ΔE CIE L*a*b* were applied in this current research.

1.12. Measurement of colour

1.12.1. Colorimeter

Colorimeters are tristimulus devices that make use of red, green, and blue filters which emulate the response of the human eye to light and colour. Colorimeters cannot compensate for metamerism. As colorimeters use a single type of light (such as incandescent or pulsed xenon) and because they do not record the spectral reflectance of the media, they cannot predict this shift. However, they represent the lowest cost answer in particular applications (Berns 2000; Mc Laren 1986).

1.12.2. Spectrophotometer

Colour measurement with a spectrophotometer involves illumination of a sample with white light, thereby calculating the amount of light that is reflected by the sample at each wavelength interval. The data is usually recorded within the visible spectrum of light for 31 wavelength intervals. The reflected light is passed through a monochromator that splits the light up into separate wavelength intervals. The obtained reflectance values are relative values and are independent of the quality and quantity of the light used to illuminate the sample (Mc Laren 1986; Schanda 2007).

1.12.3. Colour measurement for maxillofacial applications

Colorimeters and spectrophotometers have been frequently used for colour measurement in the field of maxillofacial prosthetic rehabilitation. Cantor *et al.* (1969) and Koran *et al.* (1981) both utilised reflectance spectrophotometry to

measure the colour of natural skin and observed specific spectral reflectance curves in relation to different ethnic backgrounds.

Leow *et al.* (2006) utilised a colorimeter and Paravina *et al.* (2009) a spectrophotometer when investigating colour difference thresholds for maxillofacial applications. A colour matching technique using skin coloured silicone shade guides was established by Over *et al.* (1998) based on colorimeter measurements.

More recently, Coward *et al.* (2008), Seelaus *et al*. (2011) and Nacher-Garcia (2014) used spectrophotometry in conjunction with commercially available colour formulation software when colour matching natural skin with maxillofacial elastomer for subjects of different ethnic backgrounds.

Furthermore, spectrophotometers and colorimeters have been used when investigating colour changes of elastomer following exposure to environmental conditions such as storage in darkness, accelerated ageing and natural outdoor weathering (Al-Harbi *et al.* 2015; Craig *et al.* 1978; Eleni *et al.* 2008; Gary and Smith 1998; Hatamleh and Watts 2010[a]; Kiat-Amnuay *et al.* 2009; Mancuso *et al.* 2009; Polyzois 1999; Willett and Beatty 2015).

1.13. Colour stability of maxillofacial elastomers

Silicone elastomers have become the material of choice for maxillofacial prostheses; however, the most common reason for renewal of facial prostheses is their degradation in appearance as a result of colour changes and changes of the physical and mechanical properties of silicone elastomer (Andres *et al.* 1992; Gary and Smith 1998; Lemon *et al.* 1995; Lontz 1990).

Both, non-pigmented elastomer (pure base elastomer without pigments) and pigmented silicone elastomer have been exposed to various environmental conditions including accelerated ageing, natural outdoor weathering and storage in darkness to obtain information on the colour stability of pigments and

elastomer and thereby provide estimates on the life expectancy of facial prostheses. Investigations involved the use of dry pigments, oil based and silicone based pigments, pre-blended skin tones for maxillofacial applications as well as commercially available cosmetics. Numerous research projects were conducted; however, the most relevant results are discussed in the following sections.

1.13.1. Colour stability following accelerated ageing

Beatty *et al*. (1995) and Kiat-Amnuay (2002) used dry pigments when investigating the effect of accelerated ageing on non-pigmented and pigmented A-2186 elastomer (Factor II Inc., Lakeside, Ariz.). Visible colour changes were observed in both studies; and Beatty *et al*. (1995) reported highest colour changes for the Cosmetic Red pigment with more than 55 $\overline{\Delta E}$ at the end of testing period. Kiat-Amnuay *et al*. (2002) used dry pigments in combination with kaolin as opacifier at varying concentrations; though using a different red pigment, the authors also obtained maximum $\overline{\Delta E}$ of nearly 50. However, Kiat-Amnuay *et al*. observed large improvements for the red pigment when mixed with 15% of oil-based Artskin White or the dry Titanium White pigment with approximately 17 $\overline{\Delta E}$.

Kiat-Amnuay *et al*. (2006) and Mancuso *et al.* (2009) both conducted research on the colour stability of MDX-4-4210 (Dow Corning Corp., Midland, Mich.) when exposed to accelerated ageing in a weathering chamber. Dry pigments were used for colouring by Mancuso *et al.* whereas Kiat-Amnuay *et al*. applied oil-based pigments combined with various opacifiers at different concentrations. Mancuso *et al.* reported very low colour changes of less than 1 ΔE whereas Kiat-Amnuay *et al*. reported higher values. Maximum $\overline{\Delta E}$ of 2.75 were obtained for the Cadmium Barium Red pigment combined with 15% of oil-based Titanium White pigment. However, the observed colour changes by Kiat-Amnuay *et al*. were much smaller than those observed by the authors in an earlier study (Kiat-Amnuay *et al*. 2002) which suggests that MDX-4-4210 coloured with oil-based pigments is more colour stable in the presence of UV-light than A-2186 silicone coloured with dry pigments.

Eleni *et al*. (2008) conducted research on the colour stability of ready mixed skin coloured silicone, Episil (Dreve-Dentamid GmbH, Unna, Germany), when exposed to accelerated ageing for successive 168 hours which is equivalent to seven days. This testing period is very short compared to the previously listed studies; however, the authors reported visible colour changes between 1.69 and 3.21 $\overline{\Delta E}$ after seven days only, at a total irradiation of 1.35 W m^{-2} and at a temperature between 40˚C to 45˚C. Statistically significant effects of irradiation, elastomer and their interactions ($p = 0.001$) on the colour changes of Episil were reported. These obtained results make the use of Episil for maxillofacial prosthetic applications questionable; however, this study was a very short in-vitro study and would require further investigations with prolonged testing time in order to obtain more detailed information, perhaps in form of an in-vivo study.

In 2009, Kiat-Amnuay *et al*. conducted research on the colour stability of A-2000 elastomer coloured with silicone pigments and in combination with different opacifiers at varying concentrations (Factor II). Although, the research methodology was very similar when compared with earlier studies (Kiat-Amnuay *et al*. 2002 and 2006) different elastomers and colourants were utilised. The authors reported maximum colour changes of just crossing 2 $\overline{\Delta E}$ for non-pigmented A-2000 with 5% of calcined kaolin powder and highest colour changes for the yellow silicone pigment, demonstrating $\overline{\Delta E}$ of 10.3 when combined with 5% silicone pigment white as opacifier. However, good colour stability with less than 2 ΔE was observed for a combination of pigments with all opacifiers apart from 5% calcined kaolin powder which obtained a $\overline{\Delta E}$ of 2.4. The positive outcome of an overall colour stability of combined pigments is an important result as in maxillofacial applications the combination of pigments is used in order to establish skin tones.

1.13.2. Colour stability following natural outdoor weathering

Further research on colour stability of maxillofacial elastomers has been conducted utilising natural outdoor weathering. Haug *et al.* (1999), Gary *et al.*

(2001), Hatamleh and Watts (2010[a]) as well as Al-Harbi *et al*. (2015) investigated the colour stability of A-2186 elastomer (Factor II).

Haug *et al.* (1999) included the use of dry pigments, rayon fiber flocking, oil-based pigments (artist's oil paints), kaolin (Factor II) and liquid cosmetics (Estée Lauder, New York, NY) when performing outdoor weathering of A-2186 for six months in Indiana. The authors reported highest colour changes for rayon flocking of > 4.5 $\overline{\Delta E}$ and lowest of approximately 1 $\overline{\Delta E}$ for liquid cosmetics. However, the second largest colour changes were reported for non-pigmented elastomer with 3.86 $\overline{\Delta E}$.

Gary *et al.* (2001) conducted outdoor weathering in two different locations, Florida and Arizona, and used one inorganic and two organic synthetic pigments for their study (Perma Colours, H Mark McNeal Co., Charlotte, NC) and observed lowest colour changes for non-pigmented elastomer weathered in Florida (1.11 $\overline{\Delta E}$) and highest for Alizarin Red coloured specimens weathered in Arizona (9.33 $\overline{\Delta E}$). Overall, higher colour changes were observed for specimens exposed to outdoor weathering in Arizona desert. However, the colour changes for non-pigmented specimens weathered in Arizona in this study with 3.37 $\overline{\Delta E}$ are similar to those observed by Haug *et al*. (1999) with 3.86 $\overline{\Delta E}$, where samples were outdoor weathered in Indiana.

In 2015, Al-Harbi *et al.* exposed non-pigmented silicone and silicone coloured with a preblended rose-pink shade (P409; Principality Medical, UK) to natural outdoor weathering in Saudi Arabia for six months. The results for non-pigmented specimens with 2.8 $\overline{\Delta E}$ were higher than those reported by Gary *et al.* (2001) for specimens weathered in Florida (1.11 $\overline{\Delta E}$) and lower than those observed by Haug *et al.* (1999) following outdoor weathering in Indiana (3.86 ΔE). However, the $\overline{\Delta E}$ for pigmented A-2186 with 6.68 were higher than the maximum $\overline{\Delta E}$ of 4.6 for rayon flocking observed by Haug *et al.*(1999) but lower than the maximum $\overline{\Delta E}$ of 9.33 for the dry pigment Alizarin Red as reported by Gary *et al.* (2001). Highest overall colour changes would have been expected in Saudi Arabia due to the hot climate; therefore, the observed lower $\overline{\Delta E}$ suggest

good colour stability of the pre-blended pigment mix in contrast to the dry pigment Alizarin Red used by Gary *et al*. (2001).

Hatamleh and Watts (2010[a]) and Al-Harbi *et al.* (2015) investigated the colour stability of non-pigmented TechSil S25 (Technovent Ltd., Leeds, UK) and when coloured with P409 (Principality Medical). Test samples were outdoor weathered in the UK and Saudi Arabia, respectively. Hatamleh and Watts reported maximum $\overline{\Delta E}$ of 3.89 for non-pigmented specimens in comparison to 3.00 $\overline{\Delta E}$ obtained by Al-Harbi *et al*. For pigmented specimens, 8.30 and 4.31 $\overline{\Delta E}$ were stated, respectively. These results are surprising as the same materials and similar methodology were used. Higher colour changes would have been expected for Saudi Arabia due to the hot climate; this suggests that humidity may beside temperature have a significant effect on the colour stability of elastomer. Furthermore, the colour of test samples was measured using different instruments (colorimeter and spectrophotometer) which may have contributed to the different colour change values.

1.13.3. Colour stability following darkness storage

Beatty *et al.* (1995) investigated the colour changes of A-2186 (Factor II) following darkness storage for 1800 hours. The authors observed significant $\overline{\Delta E}$ > 4.0 for non-pigmented elastomer and similar values for specimens coloured with titanium white, cadmium yellow and cosmetic red dry pigments (Factor II). Smaller colour changes of approximately 2 $\overline{\Delta E}$ were obtained for cosmetic yellow ochre; mars violet proofed being very colour stable with $\overline{\Delta E}$ < 1. The authors suggested that the observed colour changes for non-pigmented elastomer must be inherent in the elastomer as the effect of UV-light was excluded. They further stated that application of certain pigments protected the elastomer from colour changes and suggested chemical analysis in future research to better understand the underlying chemical changes resulting in observed colour changes of elastomer.

In 1999, Haug *et al*. stored non-pigmented A-2186 and the elastomer coloured with different colourants including dry earth pigments, flocking, artist's oil colours, kaolin (Factor II) and commercially available liquid cosmetic (Estée Lauder) in darkness for a period of six months. All tested colourants demonstrated maximum $\overline{\Delta E} < 1$; however, non-pigmented elastomer underwent $\overline{\Delta E}$ of 3.52. It was shown that addition of colourants decreased the elastomers' colour changes and the authors supported the concept that opacifiers could protect the silicones from colour degradation.

In a recent study, Willett and Beatty (2015) conducted research on the colour stability of A-2186 and variations of A-2186 (Factor II) in terms of durometer hardness when stored in darkness for 3000 hours. The authors measured for all tested elastomers colour changes < 1 ΔE, apart from the 5 durometer elastomer (A-221-05) which demonstrated $\overline{\Delta E}$ of 1.2.

Darkness storage for 3000 hours is equivalent to 125 days. Both, Beatty *et al.* (1995) and Haug *et al.* (1999) stated higher colour changes as a result of shorter and longer testing periods, respectively, when compared with Willett and Beatty (2015). However, Beatty *et al.* (1995) and Willett and Beatty (2015) used an aluminium mould and plastic mould, respectively; whereas Haug *et al*. (1999) utilised dental stone moulds for fabrication of silicone test specimens. Impurities in dental stone may have adversely affected A-2186 elastomer as a result of occurring side reactions within the silicone. Platinum compounds used as catalysts in addition curing silicones are especially known for their sensitivity to impurities and may have adversely affected the colour stability of the elastomer.

Hatamleh and Watts (2010[a]) exposed TechSil S25 silicone (Technovent) to darkness conditions for a period six months. $\overline{\Delta E}$ values of 6.17 and 4.72 were obtained for non-pigmented specimens and elastomer coloured with P409 (Principality Medical), respectively. The observed colour changes for non-pigmented elastomer are higher than those reported in the above studies but may be related to the longer testing period. However, Haug *et al.* (1999) reported

lower $\overline{\Delta E}$ for the same testing period which suggests that TechSil S25 is less colour stable and this may be inherent within the elastomer itself.

Bankoğlu *et al.* (2013) stored non-pigmented Cosmesil M511 and Cosmesil M522 (Principality Medical) and Mult-Epit (Bredent, Senden, Germanny) in darkness for a period of one year. The authors reported highest $\overline{\Delta E}$ of 15.36 for non-pigmented Cosmesil M511. The investigated elastomers were also intrinsically coloured with dry pigments and rayon flocking as well as extrinsic colour was applied, where white pigment added to a silicone sealant was applied on the surface of test specimens. Addition of pigments, intrinsic and extrinsic, protected all tested elastomers from colour changes. Cosmesil M511 was most colour stable with application of an extrinsic sealant layer containing the white pigment with $\overline{\Delta E}$ of 1.31. Highest $\overline{\Delta E}$ of 23.78 were reported for Cosmesil M522 when intrinsically coloured with yellow pigments. These results are high when compared with other studies on darkness storage of elastomer; however, no other research involved one year darkness storage. This testing period was a 100% time increase in comparison to other investigations and suggests that non-pigmented and pigmented elastomer both continue to undergo significant colour changes with time.

1.13.4. Other environmental effects

A facial prosthesis in clinical service is in direct contact with natural skin for extended time periods and may absorb perspiration and sebum; and these may contribute to observed colour changes of these appliances. Episil silicone (Dreve-Dentamid) was used by Polyzois *et al.* (2000) to produce test specimens which were exposed to simulated alkaline and acidic perspiration as well as to simulated sebum for a period of six months. The authors stated visually perceptible color changes for all test groups with highest $\overline{\Delta E}$ of 3.5 for samples stored in acidic perspiration and lowest $\overline{\Delta E}$ of just above 2.0 for samples stored in sebum.

Hatamleh and Watts (2010[a]) applied a similar methodology and stored non-pigmented specimens made from TechSil S25 (Technovent) and specimens

coloured with P409 (Principality Medical) in simulated acidic perspiration, sebum as well as in antimicrobial cleaning solution for six months. The authors reported that silicone cleaning solution resulted in smallest $\overline{\Delta E}$ of 1.92 for pigmented specimens. $\overline{\Delta E}$ of 6.26 were calculated for pigmented specimens stored in acidic perspiration; however, higest $\overline{\Delta E}$ of 10.78 were observed for non-pigmented samples exposed to mixed conditioning involving sebum storage and accelerated ageing in a weathering chamber.

The colour change results for non-pigmented silicone samples stored in simulated sebum were very similar when comparing the studies by Polyzois *et al.* (2000) and Hatamleh and Watts (2010[a]). However, exposure of test specimens to simulated acidic perspiration caused $\overline{\Delta E}$ values of 4.51 (Hatamleh and Watts 2010[a]) and 3.5 (Polyzois *et al.* 2000); even higher $\overline{\Delta E}$ of 6.26 were stated by Hatamleh and Watts for pigmented elastomer and may be related to the different elastomers used.

Exposure to perspiration, sebum and prosthesis cleaning solutions resulted in colour changes of facial elastomer; however, only one study involved a mixed conditioning where silicone samples were exposed to sebum storage and accelerated ageing in a weathering chamber at the same time (Hatamleh and Watts 2010[a]). Combined conditioning resulted in highest colour changes for non-pigmented and pigmented specimens of all test groups with $\overline{\Delta E}$ with 10.78 and 9.89, respectively.

These results highlight the importance of investigating multifactorial environments as they occur when a maxillofacial prosthesis is worn by a patient. All reviewed studies involved in-vitro experiments; although in-vivo studies would be more conclusive as they represent the real and everyday environments a facial prosthesis is exposed to in clinical service. Without any doubts, in-vivo studies would deliver more precise information on colour stability of maxillofacial elastomer; however, they are most challenging to conduct.

1.14. Physical and mechanical properties of maxillofacial elastomers

Silicone elastomers have become the material of choice when fabricating maxillofacial appliances; however, changes in colour and degradation of the physical and mechanical properties of silicone elastomer have been frequently reported as the main reason for renewal of maxillofacial appliances.

Today there is a large variety of maxillofacial silicones available to the clinician and numerous research investigations have been performed on the physical and mechanical properties of commercially available silicones to assess their suitability for maxillofacial applications (Aziz *et al.* 2003; Hatamleh and Watts 2010[b]; Moore *et al.*1977; Kouyoumdjian *et al*. 1985; Lai *et al*. 2002; Polyzois *et al*. 1994; Sanchez *et al*. 1992).

The assessment of physical and mechanical properties of maxillofacial elastomers following polymerisation is important to obtain information on whether the particular material is suitable for a specific maxillofacial application; however, it is vital to investigate the effect of environmental factors on the mechanical properties of elastomers. A facial prosthesis in clinical service is exposed to a variety of extra-oral conditions including UV-light, humidity, moisture as well as prolonged direct contact of elastomer to skin when the prosthesis is worn by a patient.

1.14.1. Effect of accelerated ageing

Polyzois and Andreopoulos (1993) investigated the mechanical properties of a newly developed silicone, Cosmesil HC, and compared it with Cosmesil SM4 (Cosmedica Ltd.) and Silskin II (Chas. F. Thackray Ltd., Leeds, UK) before and following accelerated ageing in a weathering chamber for a total of 200 hours. The authors observed increased tensile strength and hardness for tested elastomers and concluded moderate effects of ageing as a result of UV-light exposure on tested mechanical properties except for tear strength, where a significant decrease was observed for Silskin II and Cosmesil SM4.

Dootz *et al.* (1994) conducted research on the mechanical properties of MDX 4-4210 (Dow Corning), A-2186 (Factor II) and Cosmesil (Cosmedica) as a function of accelereated ageing. The authors reported reasonable mechanical properties of all tested elastomers before conditioning and only MDX 4-4210 remained unaffeted by accelerated ageing for all tested properties. However, it demonstrated lower tear resistance and tensile strength than A-2186 and Cosmesil. Mechanical properties of Cosmesil were more adversely affected by ageing than the other two elastomers but its tear resistance was considerably higher.

Tram-Nguyen *et al*. (2013) conducted research to evaluate the effect of two commonly used opacifiers, titanium white dry pigment, TW, and silicone intrinsic white, SW, (Factor II), and a new UV protective mineral based additive (LP; Colore Science, Dana Point, Calif.) on a pigmented mix of MDX 4-4210 and Type A medical adhesive (Dow Corning) when subjected to artificial ageing with a total irradiance of 450 kJ m^2. Artist's oil colours were used for colouring with TW and LP opacifiers, whereas silicone intrinsic colours were utilised with the SW opacifier. Statistically significant effects of opacifier, ageing and opacifier-ageing interactions on the elastomers' physical and mechanical properties were reported. Although, the TW dry opacifier is less popular than SW opacifier, the elastomer showed lowest degrees of mechanical properties degradation in combination with TW. However, considerable degradation of mechanical properties was reported for specimens with incorporated LP opacifier.

1.14.2. Effect of outdoor weathering

As shown in the previous section, accelerated ageing has been applied when investigating the mechanical properties of silicones. However, it was stated that this method may influence the elastomer degradation mechanism and could thereby lead to altered results on the materials' mechanical properties and wrong estimates on the life expectancy of elastomers in clinical service (Eleni *et al*. 2009).

Haug *et al.* (1992) conducted research on the mechanical properties of facial elastomers and included two popular used materials, A-2186 (Factor II) and MDX 4-4210 (Dow Corning). The authors exposed test specimens to outdoor weathering for six months in Indianapolis and obtained increased hardness but decreased percent elongation and tear strength for both tested elastomers. However, tensile strength was increased for A-2186 and lowered for MDX 4-4210. Haug *et al*. summarised that none of the tested elastomers met all of the desired mechanical properties values as established by Lewis and Castleberry (1980).

In 1999, Haug *et al.* investigated the effect of outdoor weathering for six months on the mechanical properties of the same elastomers as previously used and when coloured with dry earth pigments, artist's oil paints, rayon fibre flocking, kaolin (Factor II) and liquid cosmetics (Estée Lauder). No significant effects on tear strength for non-pigmented and pigmented elastomers were reported. However, there was a varying effect of colourants on tensile strength and percent elongation; these were highest for MDX 4-4210 with addition of artist's oil paints. Hardness increased for all tested elastomers but the different colourants had varying effects, with flocking resulting in highest observed hardness values. It was concluded from this study that addition of colourants altered the effect of weathering on the physical and mechanical properties of silicones.

Eleni *et al.* (2009 and 2011) investigated whether natural outdoor weathering for one year in two different locations, Thessaloniki and Athens, affected the mechanical properties of Elastomer 42, TechSil S25 (Technovent), Cosmesil M511 (Principality Medical) and an experimental chlorinated polyethylene, CPE (Department of Diagnostic Sciences, Louisville, KY). Research methodology of the above studies was the same but investigations commenced with a two months delay between them. Based on the results of both studies, the authors reported significant changes of mechanical properties of all tested materials when compared with non-weathered control specimens and related these observations to the process of photo degradation occurring during outdoor weathering.

Similar mechanical properties changes were observed in both weathering locations and are likely to be related to similar weather conditions. Eleni *et al*. further stated, tensile strength and hardness increased for Elastomer 42 and TechSil S25 but decreased for Cosmesil M511and CPE. It was suggested that as a result of photo oxidation, cross-linking took place in Elastomer 42 and TechSil S25, whereas chain scission dominated in Cosmesil M511 and CPE.

Hatamleh *et al*. (2011) performed research on the effect of outdoor weathering (Manchester, UK) on the physical and mechanical properties of TechSil S25 (Technovent) and reported significant changes. Observations included decrease in tear strength, tensile strength and percent elongation as well as increased hardness when comparing weathered with non-weathered control samples. The authors suggested that differences in the structural stability of elastomers as a result of cross-linking density caused by irradiation were the reason for the observed changes; and this was in agreement with other studies (Eleni *et al.* 2009 and 2011; Haug *et al.* 1992 and 1999).

Al-Harbi *et al.* (2015) performed outdoor weathering of TechSil S25 (Technovent), A-2186 and MED-4210 (Factor II) for six months in a hot climate (Dammam, Saudi Arabia). The authors reported decreased tear strength, tensile strength and percent elongation for TechSil S25 when comparing weathered with non-weathered control samples. This was in agreement with Hatamleh *et al.* (2011), though climate conditions were different in Dammam when compared with Manchester. This suggests a general and location independent effect of irradiation on mechanical properties of silicones though the degree of changes may vary due to different degrees of irradiation. However, TechSil S25 demonstrated highest mechanical properties for both, weathered and control samples, of all tested materials.

1.14.3. Effect of storage in darkness

Haug *et al.* (1992) looked at the effect of darkness storage (time passage) for six months on various popular maxillofacial elastomers. They reported both,

increased and decreased tear strength for the different elastomers but increased tensile strength and hardness as well as decreased percent elongation for all tested materials. Overall, the authors concluded that none of the investigated silicones met all of the recommended mechanical properties criteria as described by Lewis and Castleberry (1980). However, MDX 4-4210 and A-2186 were amongst the strongest tested maxillofacial elastomers.

In 1999, Haug *et al.* investigated the effect of time passage for six months on the physical and mechanical properties of non-pigmented A-2186 (Factor II), MDX 4-4210 and medical adhesive type A (Dow Corning) as well as when coloured with dry earth pigments, artist's oil paints, rayon fibre flocking, kaolin (Factor II) and liquid cosmetics (Estée Lauder). They stated no significant effects on tear strength but varying effects on tensile strength and percent elongation for non-pigmented and pigmented elastomers. Storage in darkness increased the hardness of all elastomers, with fibre flocking resulting in highest hardness values. Haug *et al.* highlighted that changes of mechanical properties for samples stored in darkness were unexpected and suggested that these were inherent in the elastomer and not influenced by time passage.

Hatamleh *et al*. (2011) carried out experiments on the mechanical properties of TechSil S25 (Technovent). Samples were stored in darkness for a period of six months and it was stated that tear strength, tensile strength, percent elongation and hardness decreased when comparing non-weathered control samples with specimens stored in darkness. The results of changes in mechanical properties were different to those reported by Haug *et al.* (1999) and may be related to the different materials and methodology used.

1.14.4. Other environmental effects

Lai and Hodges (1999) conducted research on the effects of processing parameters on the mechanical properties of non-pigmented and pigmented A-2186 (Factor II). Test samples were manufactured in two different mould types, stainless steel and dental stone; and were further processed using two

different curing cycles. The authors reported significantly higher tensile strength, elongation and hardness for test samples cured in stainless steel moulds when compared to those cured in dental stone moulds. It was suggested that contaminants in the dental stone may have affected the platinum catalyst and consequently the polymerisation reaction and was the reason for observed decreased mechanical properties values.

The authors further stated that incorporation of colourants (pigments dispersed in silicone fluid, kaolin and fibre flocking; Factor II) into A-2186 reduced all investigated mechanical properties. Lai and Hodges (1999) suggested that contaminants in the colourants and silicone oil, as the pigment carrier, may have been responsible for these observed changes. Curing cycles had only a significant effect on hardness with curing at higher temperature resulting in increased material hardness for both non-pigmented and pigmented A-2186, and for both mould types; it was suggested that temperature has an effect on the polymerisation reaction and resultant polymer density.

Polyzois *et al.* (2000) stated that facial prostheses in clinical service are in prolonged skin contact and may therefore absorb perspiration and sebum. The authors recognised the need to investigate the effects of the latter extra-oral conditions on the mechanical properties of maxillofacial elastomers. Test specimens were made from Episil (Drewe-Dentamid) and stored in alkaline and acidic perspiration as well as in simulated sebum for the duration of 6 months. It was concluded that simulated acidic perspiration in particular improved the mechanical properties of Episil; it was suggested that the acidic environment had a catalytic effect on the cross-linking reaction and resulted in formation of additional polymer network structures and increased mechanical properties values.

Hatamleh *et al.* (2011) exposed TechSil S25 (Technovent) to various extraoral conditions and included storage of test specimens in simulated sebum and acidic perspiration for 6 months, immersion of samples in a cleaning solution for 30 hours as well as accelerated ageing combined with sebum storage for 360 hours.

In comparison with control samples, the values of all tested mechanical properties decreased for all conditioning types except for acidic perspiration, where hardness increased; and except for storage in a cleaning solution, where percent elongation of TechSil S25 increased. It was suggested that the observed variations were based on the differences in structural stability of PDMS chains as a result of cross-linking density depending on the conditioning type.

Kheur *et al.* (2012) investigated the effect of curing mechanism on the hardness of M511 and Z004 elastomer (Technovent) when exposed to outdoor weathering for a total of nine months. Test groups included non-pigmented samples and samples coloured with a combination of dry earth pigments at 0.11 % weight (Technovent). A difference in material hardening of M511 and Z004 samples for both, room temperature and heat curing mechanisms (at unspecified temperature), was observed. Polymerisation at room temperature resulted in smaller increases in hardening over the weathering period than did heat curing and it was suggested that this may be related to the initial lower degree of polymerisation with heat cured elastomer and its more progressive polymerisation and resultant hardening during the weathering course.

Hatamleh *et al.* (2016) published a review on investigations on the physical and mechanical properties of maxillofacial elastomers over the last 45 years. The authors stated that it was difficult if not impossible to compare the results of studies as they varied in maxillofacial materials tested and in research methodology. The authors concluded that it is imperative to overcome these existing variabilities in research methodologies by establishing unified national and international standards for mechanical properties testing of maxillofacial elastomers.

1.15. Colour matching silicone elastomer to natural skin

1.15.1. Traditional method of trial and error

The traditional method of colour matching maxillofacial elastomer with natural skin describes the trial and error approach where varying colourants are added to the silicone at different concentrations and gradually until a satisfying colour match has been established. During the colouring process, the degree of colour match can be assessed by placing a small amount of coloured silicone on a polythene sheet and holding it against the skin area to be colour matched. The colour of silicone elastomer can be altered and its colour match with natural skin checked several times until all involved parties are satisfied with the degree of colour match.

Thomas (2006) describes the traditional method of colour matching as an art that requires a level of art aptitude from the clinician. He emphasises that the clinician undertaking the process of colour matching requires the ability to be able to identify and interpret colour as well as be able to recognise details. Thomas further states that these skills can only be acquired by excessive practice which ultimately leads to experience. However, this process being dependent on personal skills also makes this colour matching approach unreliable and unpredictable (Coward *et al*. 2008; Seelaus *et al.* 2011; Troppmann *et al.* 1996).

1.15.2. The use of colour match charts

Thomas (2006) described a quantitative method of traditional chair side colour matching. The author used the Cosmesil colouring system (Principality Medical) where pigments are dispersed in a liquid carrier and explained a volumetric wire dropper method for measuring pigment amounts when undertaking colour matching elastomer to natural skin. Thomas showed in detail how to accurately chart the proportions of base elastomer and pigments as a colour formula and emphasised that this technique permits repeatability of a colour formula and that

if prosthesis renewal is required at a later date, the colour formula would be readily available.

Thomas also suggested to construct silicone samples for varying colour formulae and skin tones and explained that these samples can aid in the colour matching process by choosing from a variety of skin coloured silicone samples the sample that is closest to a patient's skin colour. The colour of the selected sample can then be quickly prepared based on the predetermined pigment formula. He concludes this method can save clinical time and can be very useful for a less experienced clinician.

1.15.3. The use of skin coloured silicone swatches

Fine (1978) stated that there is no doubt that the traditional colour matching method works well for experienced and gifted individuals whose colour instinct is accurate. However, he also emphasised that acceptable colour matches have been more rapidly achieved and reproduced utilising silicone shade guides and their respective colour formulae.

A basic range of twenty skin shade guides for African subjects was fabriacted by Aina *et al.* (1978), mixing various proportions of stock colours into Silastic 399 (Dow Corning). The authors stated that a suitable series of reproducable skin shades was obtained by mixing carefully weighed proportions of stock colours with base elastomer and processing the material with a textured surface. This was achieved using a Flexistone die and allowed to impress the patient's own characteristic skin texture onto the wax pattern surface during the waxing up process. It resulted in a textured surface structure of processed elastomer, looking similar to natural skin.

Ma *et al*. (1988) recognised the fact that usually there is a colour difference between the coloured elastomer before processing and the final prosthesis. They stated that this may be related to incorporated air bubbles altering the elastomer translucency, or the change of opacity and influence of backgound colour in

relation to elastomer thickness, or the change of silicone appearance based on the difference in surface texture between the wet and glossy coloured silicone mix and the stippled matt surface of the processed material. Ma *et al*. emphasised on the effectiveness of verifying the colour of the processed prosthesis before processing the elastomer. They manufactured tapering silicone shade guides using microwave processing for 5 minutes to allow quick colour match assessments. Further colour alteration of the uncured elastomer would be still possible and this process could be repeated until a good colour match has been established.
In 1992, Godoy *et al.* produced acrylic colour shade guides for use when manufacturing acrylic facial prostheses. A total of seven colour shades with determined formulae were established utilising dry earth pigments in combination with non-fibred and pink-fibred polymer. The authors concluded that these skin shade guides would be of value to clinicians who were not completely familiar with the reproduction of skin colours in facial prosthetics.

Over *et al.* (1998) produced silicone step wedge shade guides of varying thickness (1, 2, 4, 6, 8 and 10 mm) for fifteen Caucasian subjects; and colour formulae for each shade guide were established based on volumetric measurements. The authors tested repeatability of colour formulae by producing additional two samples for three subjects, representing a light, a medium and a dark Caucasian skin tone. It was stated that duplication of silicone samples was successful with only 4 of 36 ΔE calculations being > 2. The colour match of repeated samples was also visually assessed and none of the observers could detect colour differences in any of the three presented subject silicone samples at a viewing distance of 18 inches. It was concluded that the colour formulae were consistently reproducible which is clinically very important.

Bicchierini *et al.* (2005) investigated in their study various systems used for colour matching human skin and elastomer for limb prostheses. For this research project, the authors utilised the Otto Bock colour atlas (Otto Bock Health Care GmbH, Duderstadt, Germany) which is a comprehensive silicone shade guide system for colour matching skin and nail colours in limb prosthetics. It is comprised of a large number of step wedge silicone samples, similar to those used

by Over *et al.* (1998), identified with a code; and each code being related to a respective colour formula.

Guttal *et al.* (2009) established silicone shade guides for colour matching silicone elastomer to natural skin for Indian subjects and used a similar methodology as applied by Over *et al.* (1998) and similar to the Otto Bock colour atlas (Otto Bock Health Care GmbH). Four steps wedge samples of 1, 2, 4 and 6 mm thickness were fabricated and colour formulae were established using volumetric pigment loads. The authors stated that the varying colour formulae were consistently repeatable and was in agreement with the results reported by Over *et al*. (1998).

1.15.4. Computerised colour matching method

In 1981, Koran *et al.* conducted research to measure the colour of human skin for subjects of three different ethnic backgrounds quantitatively with a spectrophotometer as a precursor to computerised selection of pigments in the manufacturing process of maxillofacial appliances. Based on the results of this study, the authors recognised the effect of different light sources on the skin colour of subjects and highlighted the importance of matching the spectral curves of skin and maxillofacial pigments in order to establish a colour match between them. They further stated that if the reflectance curve of skin would be used to match the reflectance curve of prostheses than the degree of colour match between them would be independent of the incident light and metameric effects would be minimised.

Troppmann *et al*. (1996) were the first to utilise spectrophotometry in conjunction with computerised colour formulation in the field of maxillofacial prosthetics. The authors used the Hunter Associates Laboratories colour formulation system with the included Miniscan XE spectrophotometer (Hunter Associates Laboratories Inc., Reston, Virginia); and the aim was to establish a subject's base shade based on a constant mix of silicone, A-2186, and an opacifier, kaolin (Factor II). Four ferro silicone pigments (Factor II) were utilised in this study when formulating colour recipes for five subjects of Caucasian ethnic

background. The authors stated that the difference in colour match between silicone and the actual skin reading was reduced with each iterative mix; and colour formula correction was performed by increasing pigment weights. The authors stated $\overline{\Delta E}$ of 2.9 for the final (third mix) silicone sample for all subjects and suggested that computerised colour matching represents a predictable and repeatable method.

Based on the study by Troppmann *et al.* (1996), Coward *et al.* (2008) applied colour formulation software when colour matching the skin colour of African-Canadian subjects with maxillofacial elastomer. The authors applied a technique similar to that described by Troppmann *et al.* and used the same Hunter Associates Laboratories colour formulation system in combination with the Miniscan XE spectrophotometer. An initial colour formula for each subject was defined by pigment loading (0.156%), number of pigments (4), pigment weight (0.035 g) and total weight (22.435 g). Based on this, a total of four iterative mixes were established per subject and Coward *et al.* published $\overline{\Delta E}$ of 4.48, ranging from 1.49 to 8.82 ΔE for the final silicone sample. Furthermore, only one of the 19 subjects recorded a ΔE value of less than 2.0 for the final sample, whereas Troppmann *et al.* reported ΔE values ranging from 2.25 to 3.33 for the final sample of Caucasian subjects.

Coward *et al.* (2008) also stated increased opacity of coloured elastomer with a mean pigment load of 0.59% for the final fourth silicone sample and suggested that this may compromise the clinical colour match as being too opaque. Nevertheless, the authors concluded that the system performed similarly on African-Canadian subjects to that of Caucasians in the study by Troppmann *et al*. (1996); and that colour formulation can be used as a tool to assist in managing the effects of metamerism in maxillofacial applications.

1.15.4.1. Spectromatch Pro colour formulation system

As a result of the initial studies by Troppmann *et al*. (1996) and Coward *et al.* (2008), a computerised colour formulation system, Spectromatch Pro, was

developed (Spectromatch Ltd., Bath, UK) and has become available to clinicians and is currently the only readily available software supported colour matching system for maxillofacial applications.

Spectromatch Pro utilises a spectrophotometer to measure the patient's skin colour. When recording the colour of skin, the reflected light is measured over the entire visible spectrum of light, thereby producing a spectral curve that describes the patient's real skin colour. This data is then processed to create a pigment recipe which represents a spectral match between skin coloured elastomer and skin, resulting in a non-metameric prosthesis that matches in colour with the patients'skin in all lighting conditions and to all observers. Spectromatch Ltd. emphasises that their ongoing commitment to develop ever more accurate recipe prediction algorithms has resulted in a formulation engine that accurately predicts the recipe colour when colour matching natural skin with silicone elastomer. It has been highlighted that established skin colour recipes will measure a colour difference of less than 0.8 ΔE, based on CIE ΔE in 99.8% of the time. Furthermore, with the latest version of Spectromatch Pro, recipes can be tailored to specific parameters including translucency of elastomer, addition of fibre flocking type and level; and this allows users to generate bespoke recipes that match not just in colour but appearance as well (Spectromatch 2017).

1.16. Attempts to improve the colour stability of maxillofacial elastomers

Colour changes of maxillofacial silicones have been frequently reported and UV-light has been identified as one the main effects resulting in these colour changes (Al-Harbi *et al*. 2015; Beatty *et al.* 1995 and 1999; Gary *et al.* 2001; Haug *et al.* 1999; Hatamleh and Watts 2010[a]; Polyzois 1999). As a result, attempts have been made in order to improve the colour stability of non-pigmented and pigmented maxillofacial silicones through application of UV-light absorbers and stabilisers.

1.16.1. UV-light absorbers

Chu and Fischer (1978) first investigated the effect of UV-light absorbers and one antioxidant on the colour stability of polyurethane systems and observed improved colour stability. However, polyurethanes are not used as maxillofacial prosthetic base materials and therefore research was needed for the application of silicone elastomers.

Bryant *et al.* (1994) conducted research on the colour stability of MDX-4-4210 (Dow Corning) in conjunction with commercial sunscreens which were used as a surface protective agent. Furthermore, para-amino benzoic acid (PABA; Aldrich Chemical Company Inc., Milwaukee, WI) at 5% by weight was mixed into MDX-4-4210, and all test groups were exposed to UV-light and stored in darkness for 300 hours. The results showed that none of the photo protective agents provided any significant level of UV-light protection. PABA resulted in highest colour changes of all tested materials with 17.76 $\overline{\Delta E}$ in comparison to 2.26 $\overline{\Delta E}$ for non-treated control specimens.

Lemon *et al*. (1995) incorporated a UV-light absorber (Spectra-sorb UV-5411; American Cyanamid Co.) into a mix of MDX 4-4210 and type A medical adhesive (Dow Corning) coloured with oil-based pigments and kaolin (Factor II) and exposed specimens to accelerated and outdoor weathering (150 kJ m^{-2}). The authors reported higher colour changes of silicone with added UV-light absorber (1.58 $\overline{\Delta E}$) when compared with non-treated elastomer (1.08 $\overline{\Delta E}$) and stated that this application did not protect test specimens from colour changes.

Tran *et al.* (2004) used a UV-light absorber, Tinuvin 213,in combination with a UV-light stabiliser, Tinuvin 123 (Ciba Speciality Chemicals Corp., Suffolk, VA), aiming to retard colour changes of pigmented A-2186 silicone (Factor II) when exposed to outdoor weathering in Miami (Florida) and Phoenix (Arizona). The results showed generally improved colour stability of elastomer; and lower colour changes of test specimens were observed in Phoenix. However, varying effect was noticed when comparing pigments used in this study with lower colour

changes for the Hansa Yellow pigment (organic synthetic pigment) in both weathering locations and increased colour changes for Burnt Sienna (inorganic dry pigment) in Miami and Alizarin Red (organic synthetic pigment) in Phoenix.

Han *et al.* (2013) used a UV mineral-based protecting agent (LP; Colore Science), which is a commercial cosmetic UV-light blocking powder, as an opacifier as well as dry pigments and functional intrinsic pigments (Factor II) to colour the silicone elastomer mix of MDX4-4210 and medical adhesive Type A (Factor II). Test specimens were exposed to accelerated aging in a weathering chamber (total irradiance of 450 kJ m^{-2}) and the results showed that for non-pigmented specimens, the application of UV-light absorber and addition of 15% of silicone white pigment produced small colour changes of 0.8 $\overline{\Delta E}$. However, a mix of pigments used in this study with added 5 or 15% of UV-light absorber resulted in even slightly lower colour changes of 0.7 $\overline{\Delta E}$. Smallest colour changes for pigments were obtained for red with 15% and yellow with 10% of light absorber.

In a recently published paper by Kheur *et al.* (2016), the colour stability of a maxillofacial silicone (Z004; Technovent) was investigated by adding a UV-light absorber (Chimassorb 81) and UV light stabiliser (Uvinul 5050; both BASF, India) at a concentration of 1% by weight. Test specimens were exposed to artificial ageing in a weathering chamber for 300 hours. This testing period is the same as it was used by Bryant *et al*. (1994); however, whether this represents a sufficient time period to draw any substantial conclusions on the effect of UV-light absorbers may be debatable. The results showed that the UV light absorber, Chimassorb 81, consistently showed least colour changes when compared with all other test groups and $\overline{\Delta E}$ values ranged from 0.51 to 1.11. Highest colour changes were observed for untreated elastomer specimens when exposed to artificial ageing with $\overline{\Delta E}$ of 1.48.

All of the above studies involved the application of UV-light absorbers and/or UV-light stabilisers but with varying observed colour change results. It is impossible to compare these investigations with one another due to different research methodologies. Some promising results have been stated; however,

further investigations are required especially based on standardised research protocols within the field of maxillofacial prosthetics in order to draw substantiated conclusions.

1.16.2. Surface sealing of maxillofacial elastomers

For manufacture of facial prostheses, silicone elastomer is individually coloured with pigments and fibre flocking to achieve a colour match with natural skin. In addition, extrinsic colouring is applied to highlight skin areas with specific colours. Furthermore, other characteristics such as freckles are added and covered with a thin layer of a silicone surface sealant.

Beatty *et al*. (1999) performed research on colour changes of maxillofacial elastomer investigating the colour stability of pigments only, of intrinsically coloured elastomer and non-pigmented elastomer with a coloured silicone surface sealant. The latter surface layer technique represented a method which is applied when sealing extrinsic colouring on the surface of maxillofacial prostheses.

Test specimens were stored in darkness and exposed to ultraviolet-A (UVA) and ultraviolet-B (UVB) radiation for a total of 1800 hours. The main outcome of this study was that the high pigment concentration used with the surface sealant, which was a 10-fold higher pigment concentration as used for intrinsic colouring, allowed significantly less colour changes to occur than did the thicker intrinsically pigmented silicone samples with a lower pigment concentration. The authors concluded that the obtained observations supported the use of extrinsic colouring as a protective ‘shielding’ layer against adverse UV-light related colour changes, providing adequate pigment concentration in the surface sealant layer is used and this layer remains adherent.

These observations may represent a starting point to investigate the application of extrinsic sealing methods in combination with the use of UV-light absorbers in order to improve the colour stability of silicone elastomer and consequently of maxillofacial prostheses.

1.17. Conclusions from the literature

Silicone elastomers have become the most frequently used base materials when manufacturing maxillofacial prostheses. For this particular application, the material is individually coloured with pigments and flocking in order to achieve a balanced colour match between the elastomer and a patient's natural skin.

A maxillofacial prosthesis in clinical service is exposed to a variety of environmental factors which include UV-light, humidity, moisture as well as patient related influences such as the direct and prolonged contact of elastomer with skin, handling and cleaning measures of facial appliances and personal habits such as smoking. It has been shown that the above environmental factors result in colour changes of facial prostheses and deterioration of physical and mechanical properties of maxillofacial elastomers.

However, UV-light has been determined as one of the main causes resulting in colour changes of facial prostheses and attempts have been made to utilise UV-light absorbers in order to improve the colour stability of elastomer and subsequently of facial prostheses; and some promising results have been reported.

A balanced colour match between maxillofacial elastomer and natural skin is required for successful rehabilitation of patients with facial defects. Currently, the most frequently used method of colour matching involves the arbitrary trial and error approach. However, this method is dependent upon the expertise and skills of the clinician undertaking this procedure and therefore unreliable and its results unpredictable. Furthermore, the effect of metamerism, where two coloured samples matching in one situation but not in another, cannot be controlled with this method.

The above drawbacks involved with the traditional method of colour matching led to attempts to turn this process into a quantifiable and therefore repeatable and reliable method using a scientific approach involving spectrophotometry and colour formulation software. As a result, a readily commercially available

computerised colour formulation system for maxillofacial applications has been developed; however, its suitability needs to be assessed in order to be integrated into daily clinical use.

HYPOTHESIS AND AIMS AND OBJECTIVES

2.1. Hypothesis

The colour stability and physical and mechanical properties of non-pigmented and pigmented silicone elastomer are affected by environmental conditions but colour stability can be improved through the use of UV-light absorbers and the application of a sealant layer on the surface of silicone elastomer.
When colour matching maxillofacial silicone elastomer to natural skin, colour matching based on colour formulation software achieves better results than does the traditional trial and error method; and there is no difference in colour matching results when using a spectrophotometer or colorimeter for recording of skin colour measurements.

2.2. Null hypothesis

The colour stability and physical and mechanical properties of non-pigmented and pigmented silicone elastomer are not affected by environmental conditions and colour stability cannot be improved through the use of UV-light absorbers and the application of a sealant layer on the surface of silicone elastomer.
When colour matching maxillofacial silicone elastomer to natural skin, colour matching based on colour formulation software does not achieve better results than the traditional trial and error method; and there is a difference in colour matching results when using a spectrophotometer or colorimeter for recording of skin colour measurements.

2.3. Aims and objectives of investigations

Colour changes of maxillofacial prostheses in clinical service and deterioration of their physical and mechanical properties have been frequently observed and this research project has been designed to investigate the colour stability and physical and mechanical properties of maxillofacial silicone elastomer; furthermore,

attempts have been made to increase the colour stability of silicones in order to extend the life expectancy of facial prostheses.

(i) The effect of environmental conditions on the colour stability of maxillofacial silicone elastomer will be investigated by storage in darkness of non-pigmented and pigmented silicone elastomer as well as their exposure to accelerated ageing in a weathering chamber and natural outdoor weathering for a prolonged period of time.

(ii) Non-pigmented and pigmented silicone elastomer will be stored in darkness and exposed to accelerated ageing in a weathering chamber and natural outdoor weathering for a prolonged period of time in order to see the effect on the physical and mechanical properties of the elastomer.

(iii) Experiments have been designed to investigate the use of different UV-light absorbers and the application of surface sealants on silicone elastomer samples in order to increase the colour stability of maxillofacial silicone when exposed to accelerated ageing and storage in darkness.

Traditional colour matching of maxillofacial silicone elastomer to natural skin involves the arbitrary method of trial and error; however, computer formulation has been introduced to turn the colour matching process into a reliable and repeatable process by using spectral colour measurement of skin. In this part of the study, colour measurement of skin will be performed using a colorimeter and a spectrophotometer and the recorded data will then be implemented with the computerised colour formulation software.

(iv) This part of the research has been designed to see whether colour matching based on colour formulation software produces more precise colour matches than does the traditional trial and error method.

(v) It is aimed to see whether one of the colour measurement instruments will produce more accurate colour matches when comparing the colour of maxillofacial elastomer with natural skin.

COLOUR STABILITY OF NON-PIGMENTED AND PIGMENTED M511 MAXILLOFACIAL SILICONE ELASTOMER

3.1. Introduction and aims of investigations

Today, silicone elastomers are most frequently used when manufacturing maxillofacial prostheses and are, for this particular application, individually coloured with pigments and flocking. Unfortunately, colour changes of maxillofacial prostheses in clinical service are very common and one main reason for their frequent renewal (Gary *et al*. 2001; Haug *et al*. 1999; Polyzois 1999).

As highlighted in the literature review, the colour degradation of maxillofacial prostheses has been described as a complex phenomenon and is comprised of several contributing factors which include environmental causes, personal habits of patients, the colour stability of silicone elastomer and colourants, as well as the loss of extrinsic colouration (Andres *et al*. 1992; Han *et al*. 2010; Tran *et al*. 2004).

The colour stability of non-pigmented and pigmented maxillofacial silicone elastomer has been the focus of research for decades and UV-light has been determined as one of the main factors adversely affecting the colour stability of silicones (Craig 1978; Hatamleh and Watts 2010[a]; Haug *et al*. 1992; Koran *et al*. 1979).

Despite the different materials investigated and research methodologies applied, visible colour changes of non-pigmented and pigmented maxillofacial silicone elastomer when exposed to environmental conditions were concluded (Al-Harbi *et al.* 2015; Beatty *et al.* 1995 and 1999; Hatamleh and Watts 2010[a]; Kiat-Amnuay *et al*. 2002, 2006 and 2009; Polyzois 1999). However, a most colour stable colourant and elastomer combination could not be identified.

The aim of this part of the research was to investigate the colour stability of a material combination including the HTV silicone M511 (Technovent Ltd.,

Bridgend, UK) and the Spectromatch Pro colouring system (Spectromatch Ltd., Bath, UK), where pigments were dispersed in M511 base elastomer. In order to assess the colour stability of non-pigmented and pigmented M511 silicone elastomer, test specimens were stored in darkness, exposed to accelerated ageing in a weathering chamber and natural outdoor weathering for a prolonged period of time.

3.2. Materials and methods

Five different pigment pastes (Spectromatch Ltd., Bath, UK) were investigated in this part of the study: Indian Yellow, Alizarin Crimson, Logwood Maroon, Malachite Green (organic pigments) and Me Si Green (inorganic pigment). They were used to intrinsically colour M511 maxillofacial elastomer (Technovent Ltd., Bridgend, UK). These pigment colours were chosen as they are frequently used when establishing skin colours for maxillofacial applications.

Seven test groups were designed (Fig. 3.1) and included non-pigmented M511 silicone specimens, specimens coloured with the individual pigments listed above, and a Caucasian skin tone which was established by mixing individual pigments from the Spectromatch Pro colour palette. A total of 126 silicone specimens were produced and exposed to three environmental conditions: storage in darkness, accelerated ageing in a weathering chamber and natural outdoor weathering.

The sample size of 6 specimens per test group and environment was based on previous studies (Han *et al*. 2013; Hökelmann 2008; Kiat-Amnuay *et al*. 2006 and 2009; Koran *et al*. 1979; Patel 2008).

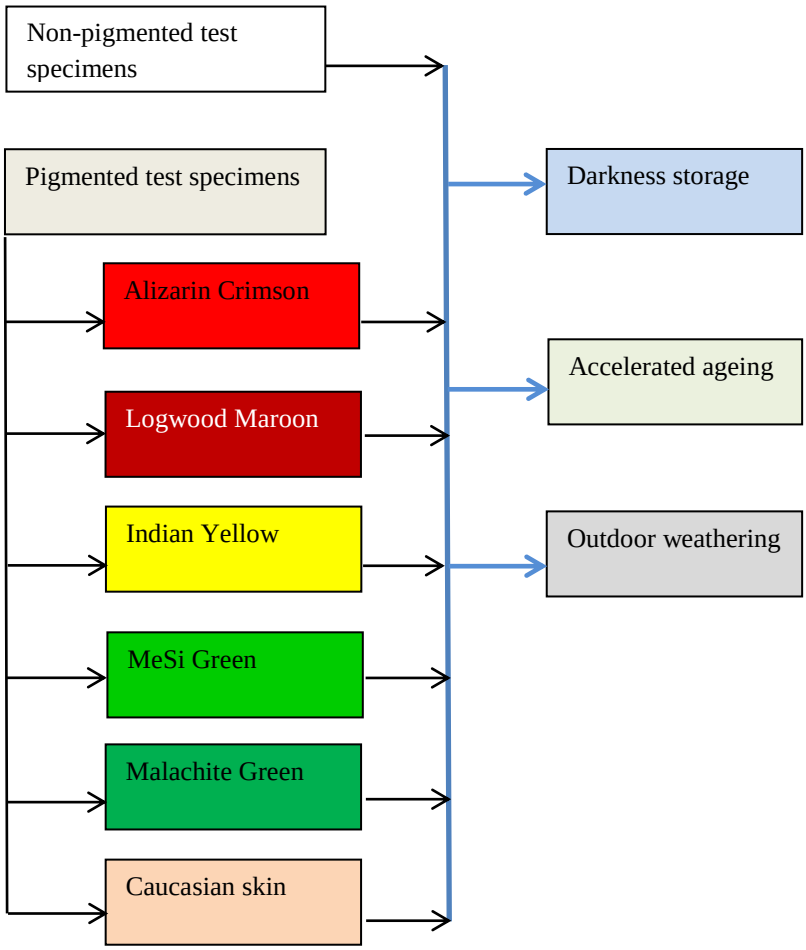


Fig. 3.1: Design of study.

3.2.1. Preparation of non-pigmented and pigmented test specimens

For manufacture of non-pigmented specimens, base polymer and cross-linker of M511 were weighed on a high precision scale (GR-120; AND Instruments, UK) in accordance to the manufacturer instructions with a ratio of 10:1, respectively. For manufacture of pigmented test specimens, a 2% weight pigment load was added. For fabrication of skin coloured test specimens, a colour recipe for a typical Caucasian skin tone was used from the skin colour data bank provided by Spectromatch Ltd. The pigments and concentration levels used for this Caucasian skin tone are listed in Appendix B (page 349). An accuracy of 0.001g was used when weighing elastomer and colourants and maintained throughout the study.

Mixing of the components was performed using the Speed Mixer DAC 150 FVZ-K (Hauschild Engineeering, Hamm, Germany) to ensure homogeneity of the mix.

Initial mixing tests were undertaken to determine an optimal time interval and speed for spatulating of the elastomer in order to achieve homogeneity of the compounds. Tests were performed at high speed and short mixing time as well as at increased time and lower mixing speed. High speed resulted in increased temperature of the elastomer-pigment mix and shortened the working time. Whereas, extended mixing at low speed did not achieve homogeneity of the elastomer-pigment mix. Based on these tests, spatulating was performed throughout the study three times for 30 seconds at 1800 rpm.

The mixed elastomer was then packed into a two piece aluminium mould containing an inner polytetrafluorethylene (PTFE) layer (Fig. 3.2). Care was taken to avoid any air entrapment. Locking screws on each side and the centre of the mould ensured that the mould remained securely closed during processing. Once filling of the mould was completed, it was closed hand tight using a wrench and then placed into a dry-heat oven (Carbolite, Thermal Engineering Services, UK). The silicone elastomer was cured at 85°C for 1.5 hours. When removed from the oven, the mould was allowed to cool down to room temperature. The test specimens were then divested and checked for any air inclusions and their dimensional accuracy using digital callipers (Electronic Digital Callipers; Order Code: N48AA, Maplin Electronics, Manvers, Rotherham, UK). All specimens were manufactured with the same dimensions of 40 mm length, 20 mm width and 8 mm thickness. They were stored in a light safe container inside a filing cabinet until the base line reading was carried out and weathering of test samples commenced.

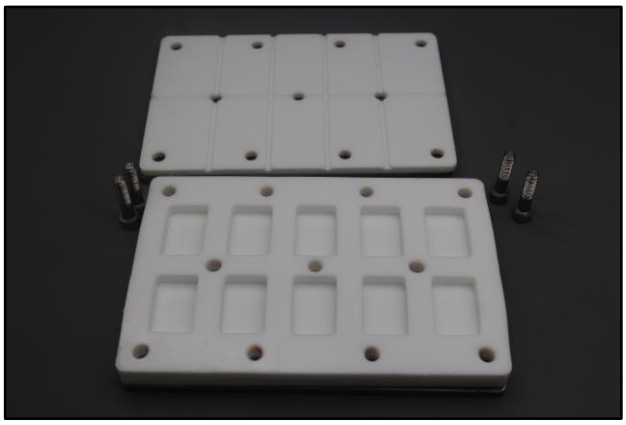


Fig. 3.2: PTFE lined aluminium mould.

3.2.2. Weathering of test specimens

Test specimens from each of the seven test groups were stored in darkness, exposed to accelerated ageing in a weathering chamber and natural outdoor weathering.

3.2.2.1. Storage in darkness

Specimens in this test group were stored in a light safe plastic container inside a filing cabinet at ambient room temperature of 21 ± 2°C and relative humidity of 38 ± 2% (Bankoğlu 2013; Beatty *et al.* 1999; Hatamleh and Watts 2010[a]; Haug *et al*. 1999). Specimens were stored in darkness for a total of successive 1500 hours, and colour was measured every 100 hours.

3.2.2.2. Accelerated ageing in a weathering chamber

Accelerated ageing in a weathering chamber represents a common method in order to assess the colour stability of maxillofacial elastomers (Eleni *et al*. 2008; Hatamleh and Watts 2010[a]; Kiat-Amnuay *et al.* 2002 and 2006). However, there is no defined standard available and individual material testing is based on

recommendations and guidelines provided by accredited companies involved in accelerated ageing testing.

The Q-Sun/1000 XENON Test Chamber (Q-Panel Lab Products, Cleveland, OH) was utilised in this study to carry out accelerated artificial weathering. All test specimens were mounted on a rack and exposed to 1.10 Wm^{-2} xenon light source with the temperature of the chamber maintained at 40°C and a black panel temperature at 63°C (Fig. 3.3). The relative humidity inside the chamber was approximately 38 ± 3% and measured using a hygrometer (Indoor-Outdoor Hygro Thermometer; code: L55AJ, Maplin Electronics, Rotherham, UK). These testing conditions were chosen based on previous MSc studies (Hökelmann 2008; Patel 2008) and papers on colour stability testing of maxillofacial silicone elastomer (Craig *et al.* 1978; Kiat-Amnuay *et al.* 2006 and 2009). All specimens were exposed to a total of successive 1500 hours of artificial ageing with colour measurements recorded at 100 hour intervals.

Fig. 3.3: Positioning of test specimens for accelerated ageing.

3.2.2.3. Natural outdoor weathering

Natural outdoor weathering was conformed to ASTM G 24-05 (ASTM 2005). The experiments were conducted utilising a glass covered cabinet constructed of wood, open on the sides to allow ambient air to circulate over the specimens. The testing enclosure was positioned with a tilt angle of 45°, facing south on the roof of a 5 storey building on the Guy's Campus, King's College London. Specimens were mounted on wooden racks which were attached to the untreated plywood backboard of the weathering cabinet (Fig. 3.4). The glass cover of the weathering cabinet was cleaned from debris at any colour assessment time interval. A summary of recorded daily weather data in London, Heathrow, for the period of outdoor weathering in this study was provided by the Met Office (Appendix C). Average monthly outdoor weathering conditions are presented in Table 3.1.

Fig. 3.4: Natural outdoor weathering of test specimens.

Month	Temperature in°C			Humidity (%)	Global Radiation (kJm^{-2})	Sunshine (hours)
	Max	Min	Average			
October 2011	18.1	10.1	14.1	76.0	7672	4.5
November 2011	13.6	7.3	10.4	87.2	3126	1.8
December 2011	9.9	3.8	6.8	81.2	2262	2.0
January 2012	9.8	3.4	6.6	80.4	2807	2.2
February 2012	8.0	1.3	4.6	76.7	5473	2.9
March 2012	14.7	4.7	9.7	73.6	10971	5.8
April 2012	13.3	4.9	9.1	74.5	12973	4.7
May 2012	18.2	9.7	13.9	72.2	16185	5.4
June 2012	19.4	11.6	15.5	74.5	15581	4.0

Table 3.1: Monthly average climate data and radiation during outdoor weathering.

All test specimens were exposed to a total of 1500 hours of daylight. This was calculated based on the time of sun rise and sun set for every day during the testing period. Samples were collected from the outdoor weathering cabinet after every 100 hours of daylight had elapsed for colour measurement. This procedure was repeated until a total of 1500 hours of outdoor weathering was completed.

3.2.3. Measurement of colour and calculation of colour change

Prior to colour measurement, test specimens were cleaned with a mild detergent (Procter & Gamble, Weybridge, UK) and distilled water in order to remove any debris from the surface as it could adversely affect the colour measurement. They were then wiped dry and conditioned at a room temperature of 21 ± 2°C for 30 min before colour measurements were carried out. Reflectance spectrophotometry was applied to assess the colour of test specimens for all testing conditions at base line (0 hours) and then every 100 hours until a total of 1500 hours was completed. Prior to measuring at any time period, the spectrophotometer (CM-2600d; Konica Minolta Sensing, Japan) was calibrated

according to the manufacturer instructions by using the supplied white calibration standard.

The spectrophotometer setting for this study involved a D65 standard illuminant which represents the average midday daylight in Western/Northern Europe and comprises of both, direct sunlight and light diffused by a clear sky, and has a correlated colour temperature of approximately 6500 K (Hunt and Pointer 2011). The instrument viewing geometry was set at 8° and a 10° standard observer, Specular Component Included (SCI) mode. A measuring head aperture of 8 mm was used (Fig. 3.5), and a xenon flash light diffusely illuminated the samples to be assessed. All test specimens were measured three times over a white standard background (W) and three times over a black standard background (B) which represents an accredited methodology in colour stability testing and has been applied by various authors (Hulterström and Ruyter 1999; Koran *et al.* 1979; Turner *et al*. 1984). Specimens were mounted in a specially designed sample holder to ensure colour measurements were taken in exactly the same space for every single colour measurement (Fig. 3.6).

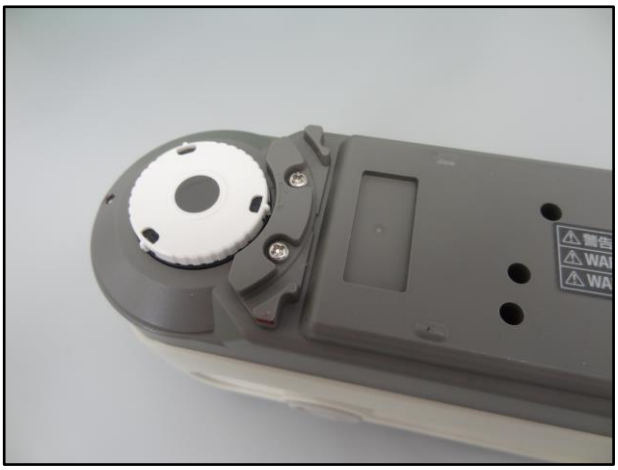


Fig. 3.5: Measuring head aperture of the spectrophotometer.

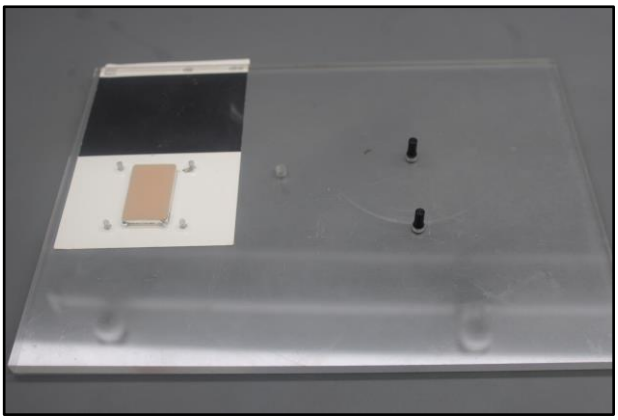


Fig. 3.6: Specially designed sample holder for colour measurement.

The recorded L*a*b* values were generated using the Colibri software (CIBA, Cheshire, UK) and entered onto an Excel worksheet (Microsoft Corporation, Redmond, WA, USA). The colour change values (ΔE) for each test specimen were calculated using the following equation:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5}$$ (ASTM 1989)

3.2.4. Statistical analysis

The statistical analysis of the data was computed with Stata 14.2., Stata Statistical Software: Release 14, College Station, Tx. (Stata Corp. 2016). Statistical significance was predetermined at $\alpha = 0.05$ for all hypothesis tests. As each specimen was measured three times at 15 time periods the results are repeated measures and the data is correlated; to allow for this, the effect of time, pigment, background and environment were analysed using linear mixed models (Rabe-Hesketh and Skrondal 2008; West *et al.* 2007). Where appropriate, Šídák's multiple comparison of means test was used in the comparison of groups (Šídák 1967).

3.3. Results

All colour measurements of test samples and corresponding calculated colour differences ($\overline{\Delta E}$) for this part of the study are provided in Appendix D. The colour stability of non-pigmented and pigmented M511 silicone elastomer was adversely affected by darkness storage, exposure to accelerated ageing in a weathering chamber and natural outdoor weathering. For all test specimens and environments, there was a significant effect of time on the $\overline{\Delta E}$ ($p = 0.001$) of all test samples for both, black (B) and white (W) backgrounds.

An initial analysis involving all independent variables showed all main factors to be statistically significant together with several of the interactions (Table 3.2). This makes a meaningful interpretation of the data difficult and consequently the data was split by background. The results for pairwise comparison of environments per background are summarised in Table 3.3.

Factor	p
Time	0.001
Pigment	0.001
Environment	0.048
Pigment # environment	0.001
Background	0.021
Pigment # background	0.065
Environment # background	0.490
Pigment # environment # background	0.962

Table 3.2: Summary of mixed model analysis for the dependence on $\overline{\boldsymbol{\Delta E}}$ on all the independent variables and their interactions (#).

Pigment	Background					
	Black			White		
	p (D-O)	p (D-A)	p (O-A)	p (D-O)	p (D-A)	p (O-A)
Caucasian skin tone	0.001	0.001	0.001	0.001	0.001	0.001
Logwood Maroon	0.005	0.001	0.001	0.006	0.001	0.001
Indian Yellow	0.986	0.001	0.001	0.615	0.001	0.001
Alizarin Crimson	0.559	0.001	0.001	0.412	0.001	0.001
MeSi Green	0.469	0.256	0.063	0.300	0.460	0.076
Non-pigmented	0.001	0.001	0.001	0.001	0.001	0.001
Malachite Green	0.241	0.001	0.001	0.006	0.001	0.001

Table 3.3: Probabilities, p (), for the pairwise comparison of environments (D-O, D-A, O-A) for each pigment, background combination.

(Legend: p (D-O) Darkness-Outdoor, p (D-A) Darkness-Accelerated, p (O-A) Outdoor-Accelerated)

Šídák's multiple comparison of means test was applied for comparison of pigments within each environment, background combination and results are summarised in Table 3.4.

Environment	Pigment	Background	
		Black	White
Darkness	Caucasian skin	B	A
	Logwood Maroon	B	A
	Indian Yellow	A	CD
	Alizarin Crimson	A	DE
	MeSi Green	C	B
	Non-pigmented	A	E
	Malachite Green	AC	BC
Accelerated Ageing	Caucasian skin	AD	C
	Logwood Maroon	B	A
	Indian Yellow	A	
	Alizarin Crimson	CD	BC
	MeSi Green	B	A
	Non-pigmented	A	
	Malachite Green	C	B
Outdoor Weathering	Caucasian skin	A	CD
	Logwood Maroon	C	BC
	Indian Yellow	AB	AD
	Alizarin Crimson	B	A
	MeSi Green	C	B
	Non-pigmented		
	Malachite Green	AB	A

Table 3.4: Šídák's multiple comparison of pigments for each environment, background combination over the entire exposure period.

Pigments sharing the same letter are not statistically significantly different.

3.3.1. Darkness storage

For all test specimens, there was a significant effect of time on the ΔE ($p = 0.001$) for both backgrounds. When measured over both backgrounds, there was no statistically significant difference for Malachite Green and Logwood Maroon coloured test specimens. Caucasian skin and Logwood Maroon demonstrated the lowest colour changes of all test groups after 1500 hours with 0.19 $\overline{\Delta E}$ (W) and 0.15 $\overline{\Delta E}$ (W) and 0.19 $\overline{\Delta E}$ (B) and 0.14 $\overline{\Delta E}$ (B), respectively.

Alizarin Crimson, Indian Yellow and non-pigmented specimens exceeded the PT when measured over the white background. When measured over the black background, the same effect was observed for Alizarin Crimson and Indian Yellow. The largest colour change values were observed for Indian Yellow coloured specimens after 1400 hours with 1.75 $\overline{\Delta E}$ (W) and 1.62 $\overline{\Delta E}$ (B) but remained well below the AT of 2 ΔE.

The $\overline{\Delta E}$ and standard deviation for each background and pigment combination at 1500 hours, and the probability, p, that $\overline{\Delta E}$ is the same at each time period is summarised in Table 3.5.

Environment	Pigment	Black		White	
		1500 h		1500 h	
		$\overline{\Delta E}$, sd	p	$\overline{\Delta E}$, sd	p
Darkness	Caucasian skin	0.19, 0.04	0.001	0.19, 0.05	0.001
	Logwood Maroon	0.14, 0.04	0.224	0.15, 0.04	0.390
	Indian Yellow	1.26, 0.34	0.001	1.31, 0.35	0.001
	Alizarin Crimson	1.01, 0.66	0.001	1.24, 0.19	0.001
	MeSi Green	0.66, 0.08	0.002	0.70, 0.09	0.001
	Non-pigmented	0.76, 0.06	0.529	1.16, 0.34	0.014
	Malachite Green	0.51, 0.14	0.914	0.56, 0.17	0.404

Table 3.5: Univariate summary statistics for $\overline{\Delta E}$ after 1500 hours exposure in a dark environment for all pigment and background combinations, and the probability, p, associated with the difference in$\overline{\Delta E}$ between 100 and 1500 hours.

The $\overline{\Delta E}$ values and associated 95% confidence intervals for all test specimens at each time period and background are illustrated in Figs. 3.7 and 3.8. In these figures, the perceptibility threshold (PT) of 1 ΔE and the acceptability threshold (AT) of 2 ΔE are shown as horizontal lines.

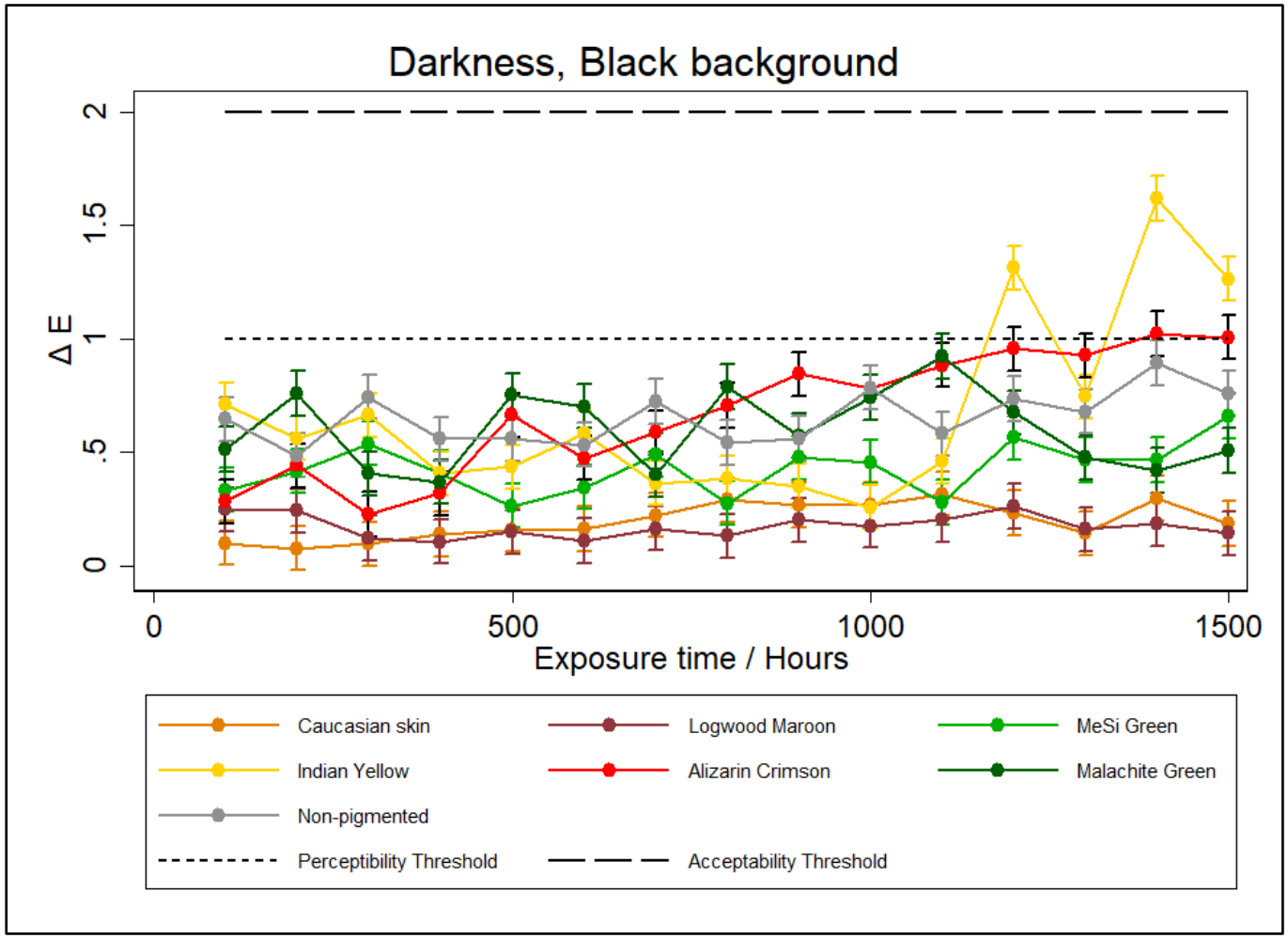


Fig. 3.7: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

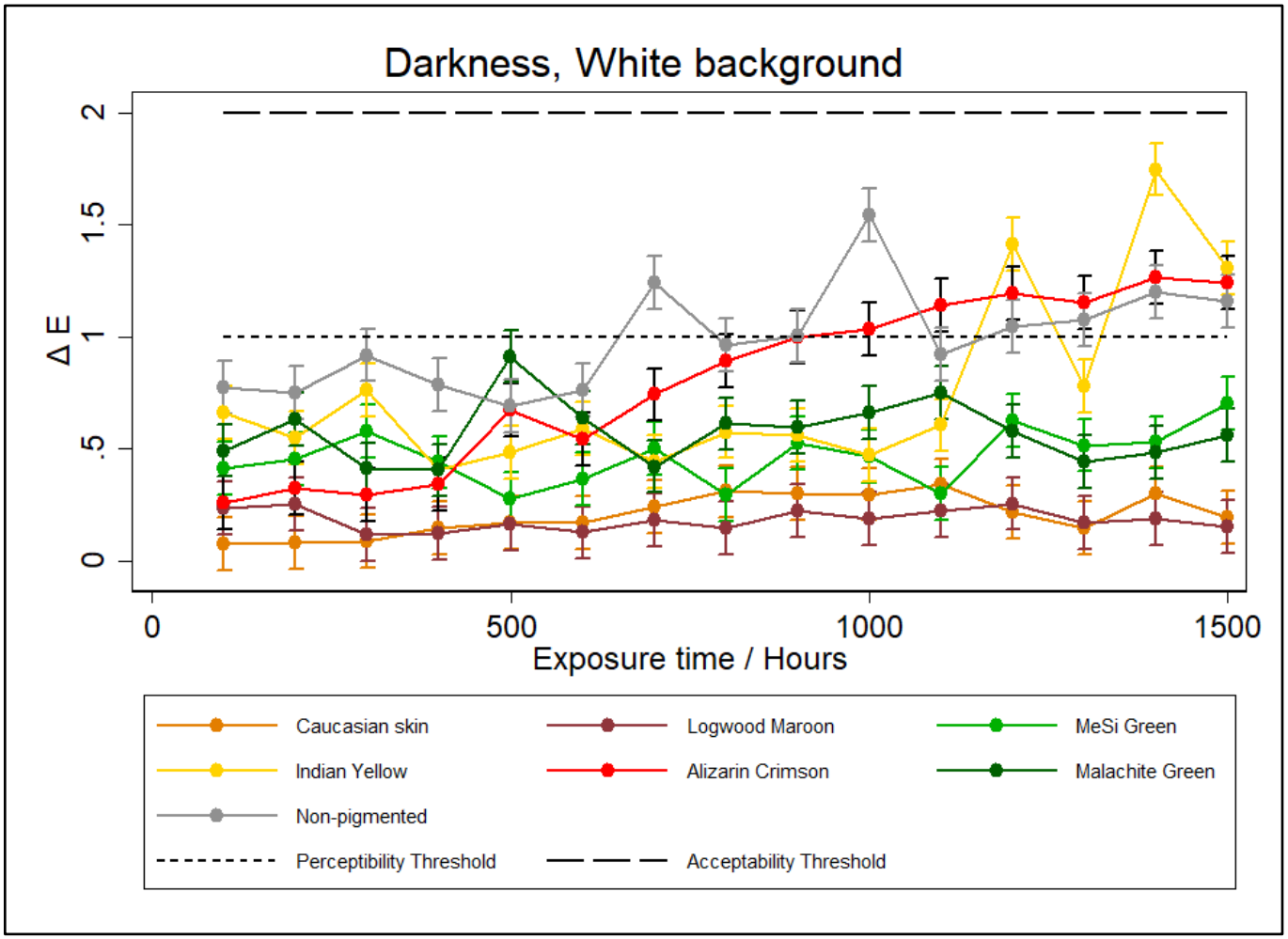


Fig. 3.8: $\overline{\mathbf{\Delta E}}$ values and associated 95% confidence interval at each time period.

3.3.2. Accelerated ageing

There was a significant effect of time on the ΔE (p = 0.001) of all test samples for both backgrounds. The recorded data was very scattered. However, when measured over both backgrounds, Indian Yellow, Caucasian skin, non-pigmented, Alizarin Crimson and Malachite Green exceeded the AT of 2 ΔE. Highest colour change values were measured for Indian Yellow after 1500 hours with $\overline{\Delta E}$ of 5.20 (W) and 4.88 (B).

When measured over both backgrounds, there was no statistically significant difference for MeSi Green and Logwood Maroon coloured test specimens. Smallest colour change values were observed for Me Si Green and the PT of 1 ΔE was only crossed after 1400 hours.

The $\overline{\Delta E}$ and standard deviation for each background and pigment combination at 1500 hours, and the probability, p, that $\overline{\Delta E}$ is the same at each time period is summarised in Table 3.6.

Environment	Pigment	Black		White	
		1500 h		1500 h	
		$\overline{\Delta E}$, sd	p	$\overline{\Delta E}$, sd	p
Accelerated Ageing	Caucasian skin	3.25, 0.67	0.001	3.26, 0.67	0.001
	Logwood Maroon	0.72, 0.16	0.053	0.74, 0.17	0.079
	Indian Yellow	4.88, 0.49	0.001	5.20, 0.35	0.001
	Alizarin Crimson	2.38, 0.26	0.001	2.50, 0.25	0.001
	MeSi Green	1.16, 0.26	0.001	1.21, 0.27	0.001
	Non-pigmented	2.99, 0.39	0.001	4.86, 0.13	0.001
	Malachite Green	2.35, 0.30	0.001	2.57, 0.25	0.001

Table 3.6: Univariate summary statistics for $\overline{\Delta E}$ after 1500 hours exposure to accelerated ageing for all pigment and background combinations, and the probability, p, associated with the difference in $\overline{\Delta E}$ between 100 and 1500 hours.

The $\overline{\Delta E}$ values and associated 95% confidence intervals for all test specimens at each time period and background are illustrated in Figs. 3.9 and 3.10. In these figures, the perceptibility threshold (PT) of 1 ΔE and the acceptability threshold (AT) of 2 ΔE are shown as horizontal lines.

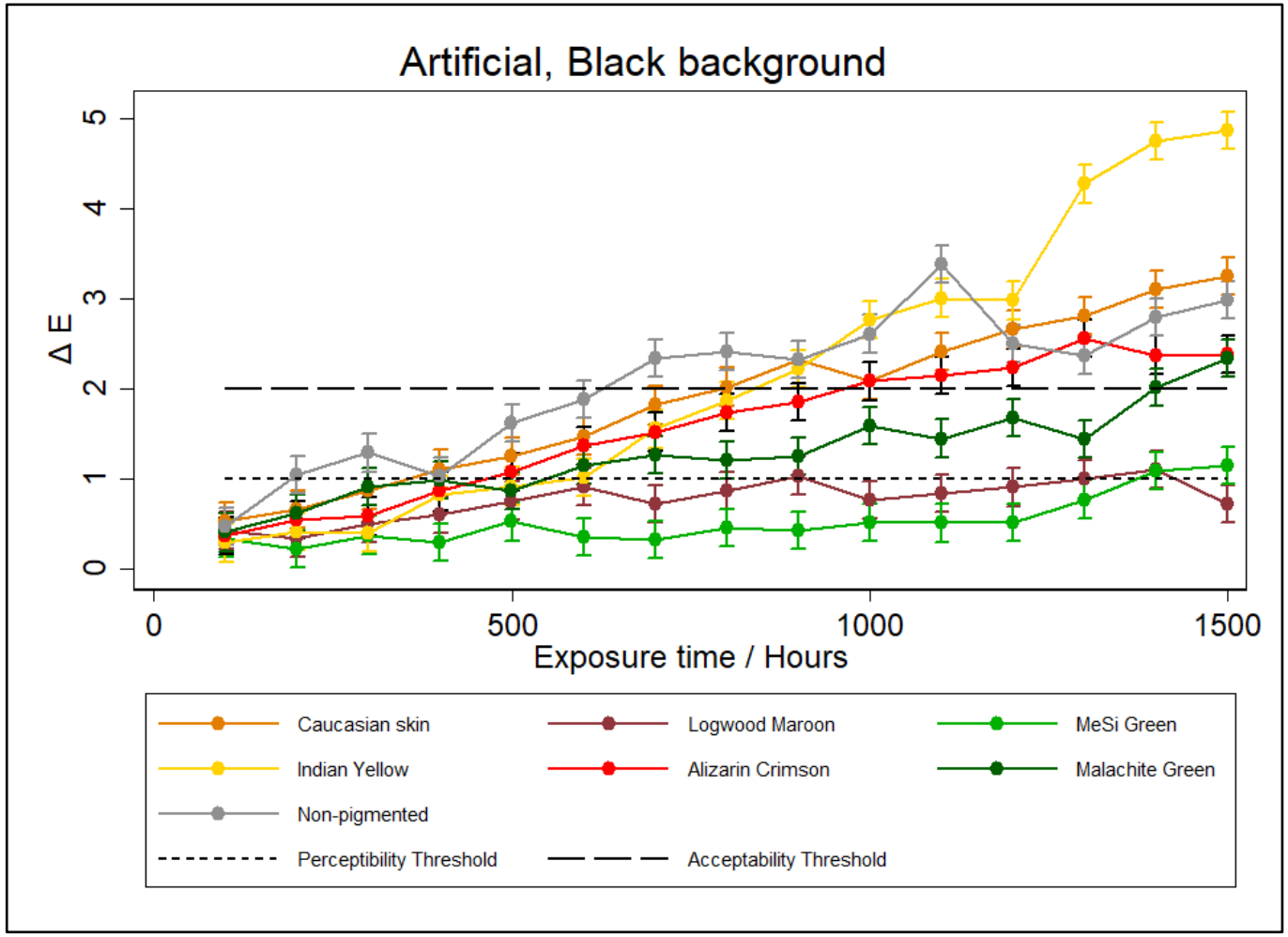


Fig. 3.9: $\overline{\mathbf{\Delta E}}$ values and associated 95% confidence interval at each time period.

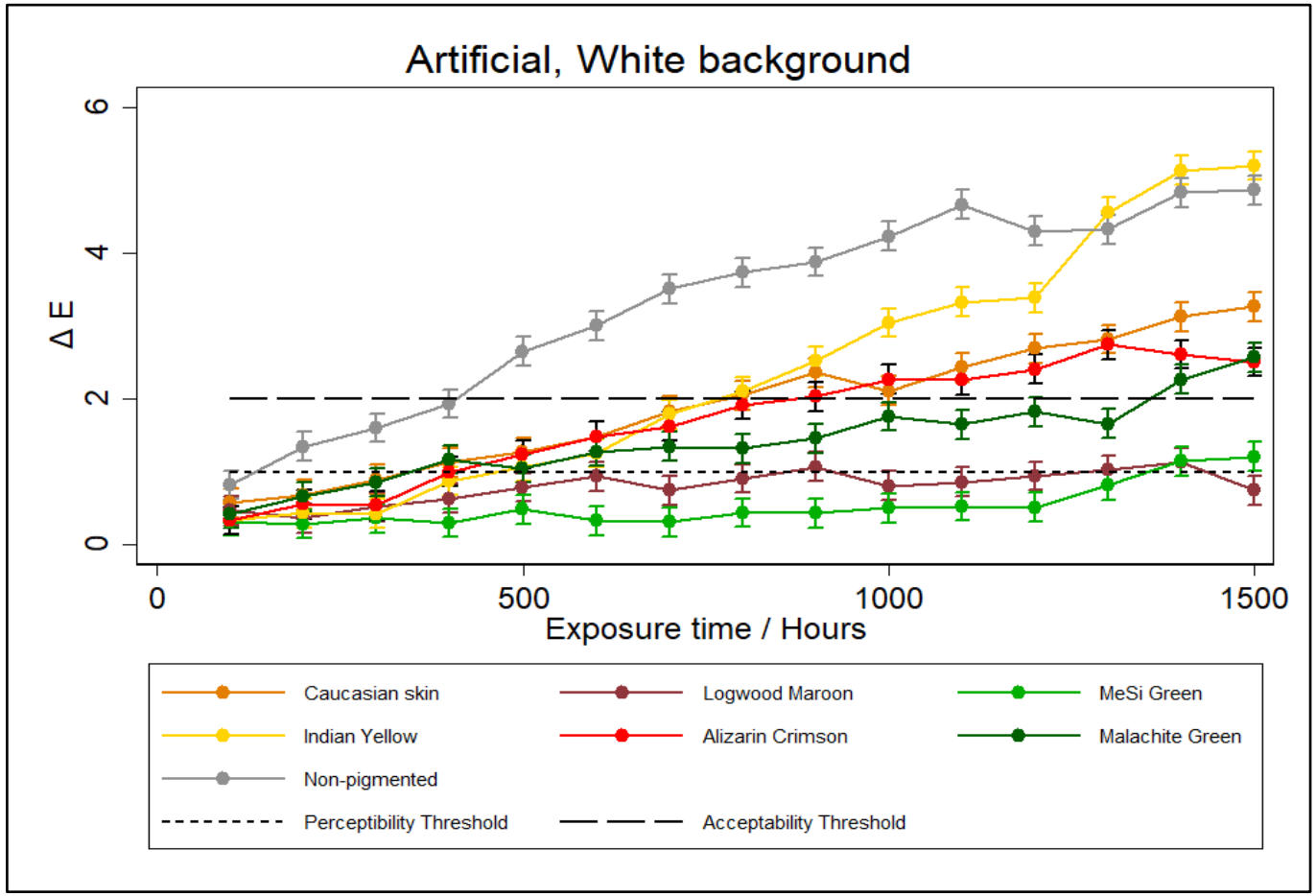


Fig. 3.10: $\overline{\mathbf{\Delta E}}$ values and associated 95% confidence interval at each time period.

3.3.3. Natural outdoor weathering

There was a significant effect of time on the ΔE (p = 0.001) of all test samples for both backgrounds. When measured over both backgrounds, there was no statistically significant effect for MeSi Green coloured test specimens. Non-pigmented, Alizarin Crimson and Caucasian skin exceeded the PT of 1ΔE when assessed over both backgrounds. Malachite Green coloured specimens exceeded the PT only at 1100 hours of outdoor weathering.

Highest colour change values were measured after 1500 hours for non-pigmented test specimens with $\overline{\Delta E}$ of 2.42 (B) and 3.65 (W). Lowest $\overline{\Delta E}$ values were calculated for Me Si Green with 0.38 (B) and 0.39 (W).

The $\overline{\Delta E}$ and standard deviation for each background and pigment combination at 1500 hours, and the probability, p, that $\overline{\Delta E}$ is the same at each time period is summarised in Table 3.7.

Environment	Pigment	Black		White	
		1500 h		1500 h	
		$\overline{\Delta E}$, sd	p	$\overline{\Delta E}$, sd	p
Outdoor Weathering	Caucasian skin	1.23, 0.17	0.001	1.26, 0.15	0.001
	Logwood Maroon	0.66, 0.04	0.001	0.66, 0.05	0.001
	Indian Yellow	0.78, 0.15	0.021	0.51, 0.09	0.037
	Alizarin Crimson	1.22, 0.08	0.001	1.48, 0.09	0.001
	MeSi Green	0.38, 0.06	0.349	0.39, 0.06	0.296
	Non-pigmented	2.42, 0.12	0.001	3.65, 0.19	0.001
	Malachite Green	0.85, 0.10	0.001	1.04, 0.09	0.001

Table 3.7: Univariate summary statistics for $\overline{\Delta E}$ after 1500 hours exposure to outdoor weathering for all pigment and background combinations, and the probability, p, associated with the difference in $\overline{\Delta E}$ between 100 and 1500 hours.

The $\overline{\Delta E}$ values and associated 95% confidence intervals for all test specimens at each time period and background are illustrated in Figs. 3.11 and 3.12. In these

figures, the perceptibility threshold (PT) of 1 ΔE and the acceptability threshold (AT) of 2 ΔE are shown as horizontal lines.

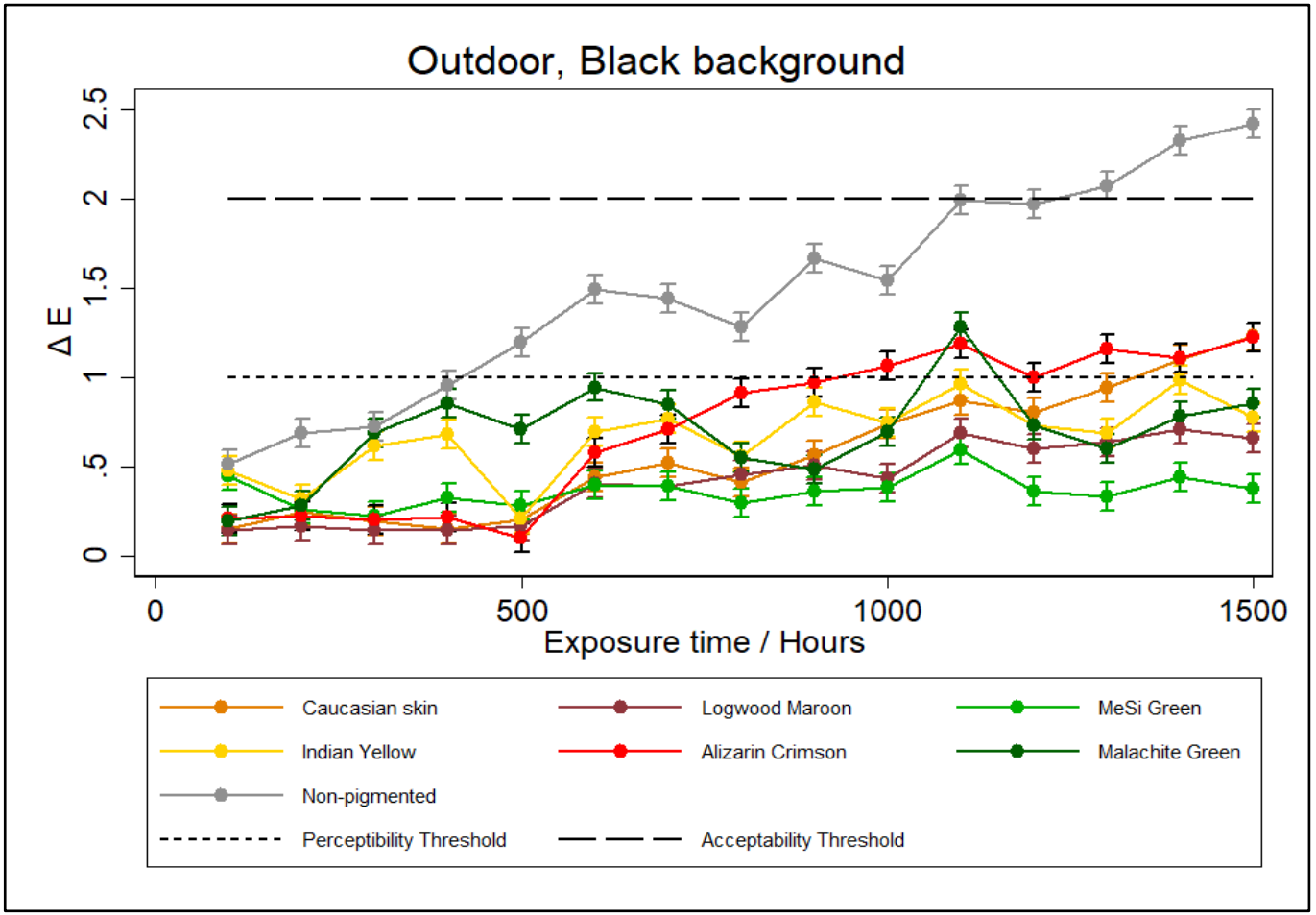


Fig. 3.11: $\overline{\mathbf{\Delta E}}$ and associated 95% confidence interval at each time period.

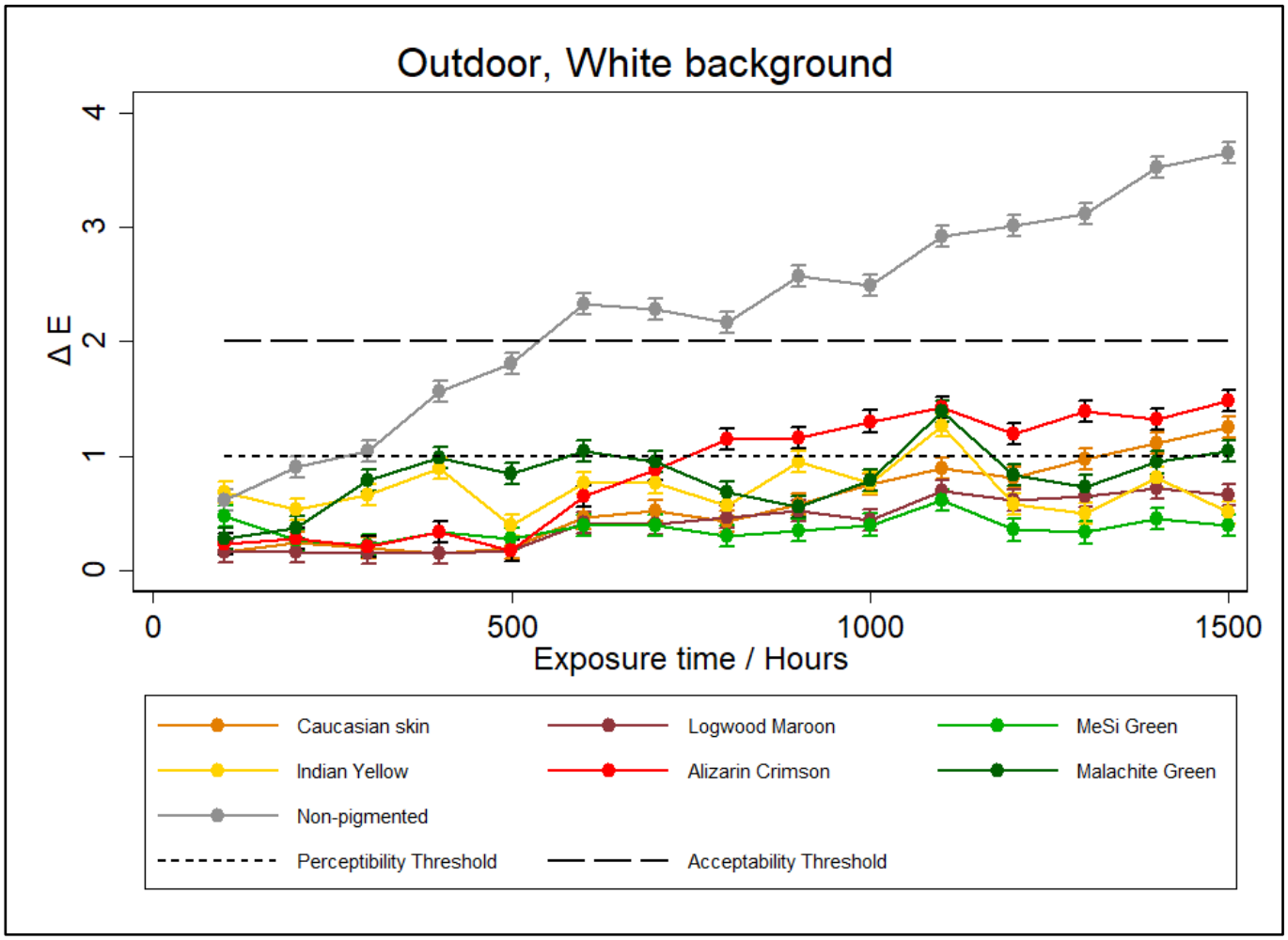


Fig. 3.12: $\overline{\mathbf{\Delta E}}$ and associated 95% confidence interval at each time period.

3.4. Discussion

It is a known fact that maxillofacial prostheses exhibit two major clinical limitations which include their gradual discolouration in a service environment and degradation of physical and mechanical properties (Craig *et al*. 1978; Gary *et al*. 2001; Hatamleh and Watts 2010 [a]; Eleni *et al.* 2011). In 1978, Jani and Schaaf reported that approximately one third of annual facial prostheses renewals were related to their discolouration. Whereas, Hatamleh *et al*. (2010[c]) who performed a survey with maxillofacial prosthetists and technologists in the UK stated that 71.4% of annual provision of prostheses were required as a result of prosthesis discolouration.

This part of the study was designed to investigate the colour stability of test specimens made from M511 silicone (Technovent). The material was tested in a non-pigmented state and when intrinsically coloured with Spectromatch Pro colourants (Spectromatch). Four different organic, one inorganic pigment and a combination of pigments resulting in a Caucasian skin tone were investigated when storing test specimens in darkness and exposing them to accelerated ageing in a weathering chamber and natural outdoor weathering for a period of 1500 hours. The results showed that all non-pigmented and pigmented test specimens underwent varying amounts of colour changes regardless of the environment. Accordingly, we reject the null hypothesis for this part of the study.

Various perceptibility thresholds (PT) and acceptability thresholds (AT) have been reported in dentistry and in relation to maxillofacial prosthetics. However, throughout this study, the colour changes of M511 were evaluated based on the PT of 1 ΔE and AT of 2 ΔE. These represent values based on investigations performed by Kuehni and Marcus (1979) and Seghi *et al.* (1989). Kuehni and Marcus found that a ΔE of 1 was detectable by 50% of the observers in this study, whereas Seghi *et al.* (1989) looked at the relationship between calculated colour difference values and human observer responses involving translucent dental porcelain and stated that a ΔE of 1represents a colour difference that is

perceivable for the average dental observer group; and that a colour difference greater than 2 ΔE was correctly judged by the observer group 100% of the time.

In the field of body and facial prosthetics, Leow *et al*. (2006) and Paravina *et al.* (2009) published different PT and AT values. For fair skin, a PT of 0.8 ΔE and 1.1 ΔE was published and was similar to the PT of 1 stated by Kuehni and Marcus (1979). However, the AT ranged from 1.8 ΔE for fair skin to 4.4 ΔE for dark skin.

Furthermore, spectral measurements were obtained over a black (B) and over a white (W) calibration standard background; this has been used in the literature when assessing colour differences. The white calibration standard represents a 100% reflective background, whereas the black background is 100% light absorbing. This colour assessment procedure represents an accredited methodology in colour stability testing of maxillofacial elastomers (Hulterström and Ruyter 1999; Koran *et al.* 1979; Turner *et al*. 1984).

3.4.1. Colour stability following storage in darkness

3.4.1.1. Non-pigmented specimens

It was observed from the results that non-pigmented silicone elastomer demonstrated $\overline{\Delta E}$ values ranging from 0.76 (B) to 1.16 (W) after 1500 hours of darkness storage. Specimens underwent colour changes that were just visually perceptible with $\overline{\Delta E}$ values ≥ 1 but well below the AT of 2 ΔE.

Beatty *et al*. (1995) investigated the colour changes of non-pigmented A-2186 (Factor II) and a 70 : 30% mix of non-pigmented 891 Type A adhesive (Dow Corning) under darkness conditions and stated colour changes larger than 4 ΔE and of approximately 2 ΔE, respectively. These results are significantly higher than the colour changes observed in the current study and may be inherent in the elastomer itself. Haug *et al*. (1999) tested Silastic medical adhesive type A,

Silastic 4-4210 (Dow Corning) and A-2186 (Factor II) for the duration of six months and stated all tested elastomers demonstrated colour changes smaller than 1 ΔE, with Silastic 4-4210 being the most colour stable. These observations are similar to those recorded in this current study.

Hatamleh and Watts (2010[a]) stored specimens fabricated from TechSil S25 silicone (Technovent) in darkness also for a period six months. In both studies, Haug *et al*. (1999) and Hatamleh and Watts, specimens were fabricated in stone moulds; however, the results of the study by Hatamleh and Watts demonstrated much higher colour changes ($\overline{\Delta E}$ of 6.17) which may be related to the material itself, with Techsil being more sensitive to impurities.

Bankoğlu *et al.* (2013) investigated the colour stability of non-pigmented Cosmesil M511, the same elastomer as used in this current study, as well as Cosmesil M522 (Principality Medical) and Mult-Epit (Bredent, Senden, Germanny). The authors exposed specimens to darkness for a period of one year and observed large colour changes, M511 demonstrating $\overline{\Delta E}$ values of 15.36. This is very different from the observed results in this current study and may be related to the use of dental stone moulds by Bankoğlu *et al*. in comparison to PTFE lined moulds in this current study.

Despite using different research methods, the observed colour changes of non-pigmented specimens stored in darkness in this current study were similar to those reported by Haug *et al*. (1999). The findings from all five studies suggest that the observed colour changes were inherent in the elastomers as the known effect of UV radiation was excluded. It has been indicated that these colour changes may have been caused by continued chemical polymerisation of the silicone or by side reactions among impurities present within the silicone.

Platinum compounds used as catalysts in addition curing silicones are especially known for their sensitivity to impurities (Haug *et al*. 1999; Hatamleh and Watts 2010 [a]). A PTFE mould was used in this current study to prevent any influence caused by impurities and may have been a reason for the observed smaller colour

changes. However, no compositional analysis was conducted and the true underlying mechanism for colour changes of non-pigmented elastomer specimens stored in darkness is still unknown and requires further research.

3.4.1.2. Pigmented test specimens

The results of this part of the study showed that most pigmented test specimens demonstrated good colour stability with maximum colour changes below the PT of 1 ΔE. Only Alizarin Crimson and Indian Yellow pigmented specimens showed maximum $\overline{\Delta E}$ of 1.24 (W) and 1.31 (W), respectively.

Beatty *et al.* (1995) studied the colour changes of A-2186 elastomer coloured with five different dry earth pigments (Factor II) when stored in darkness and stated maximum colour changes larger than 4 ΔE. These results are in contrast to the observations obtained in the current study and may be related to the choice of pigments and elastomer. The known negative effect of UV-light on the colour stability of pigments and elastomer was excluded in this experiment and incompatibility between elastomer and pigments may have contributed to the observed colour changes. However, a chemical analysis was not performed to substantiate this statement.

Beatty *et al.* (1995) stated that only one pigment, Mars Violet, remained colour stable throughout the testing period with maximum colour changes below the PT of 1 ΔE which supports the authors' statement that certain pigments are more colour stable than others when combined with silicone elastomer.
In a later study, Beatty *et al*. (1999) conducted research on the colour stability of oil-based pigments mixed into a made up elastomer containing 70% of 891 Type A adhesive (Dow Corning) and 30% of A-2186 (Factor II). The authors reported that oil-dispersed pigments demonstrated higher colour changes between 4 and 7 ΔE, which indicates an unfavourable chemical effect of oil on the colour stability of pigments.

Haug *et al*. (1999) investigated the colour stability of different colourants which included dry earth pigments, flocking, artist's oil colours, kaolin (Factor II) and a commercially available liquid cosmetic (Estée Lauder). Apart from artist's oil pigments mixed into Silastic Medical Adhesive Type A (Dow Corning), all tested colouring agents when mixed into Medical Adhesive Type A, Silastic 4-4210 (Dow Corning) and Silicone A-2186 (Factor II) demonstrated maximum colour changes below the PT of 1 ΔE under darkness conditions. The colour changes stated in this study were similar to the results observed in this current study. Hatamleh and Watts (2010 [a]) intrinsically coloured TechSil S25 (Technovent) with a pre-blended rose-pink skin shade (P409; Principality) and stored specimens in darkness for six months and stated higher $\overline{\Delta E}$ values of 4.72.

Extreme colour changes were reported by Bankoğlu *et al*. (2013) when storing coloured Cosmesil M511 and M522 (Principality) in darkness for one year. They reported lowest colour changes for the tested white dry pigment mixed into M522 with colour changes of 7.1 $\overline{\Delta E}$. However, they also observed highest $\overline{\Delta E}$ values of 21.61 and 23.78 for specimens made for M511 and M522 when coloured with the dry yellow pigment. These results are in great contrast with observations made in this current study and the studies by Beatty *et al.* (1995) and Haug *et al.* (1999). The difference in research methodology makes a direct comparison of all studies impossible. Haug *et al*. (1999), Hatamleh and Watts (2010 [a]) and Bankoğlu *et al*. (2013) all manufactured test specimens in stone moulds but Beatty *et al*. (1995) used aluminium moulds with an applied PTFE coating separator. In this current study specimen were produced using a PTFE mould.

The choice of mould in this study may be one reason for the observed lower colour changes of pigmented silicone elastomer as impurities that could chemically affect the maxillofacial silicone and pigments were excluded. Further, only baseline and final colour change readings instead of measurements at time intervals were recorded in the above mentioned studies which make a cross-comparison of colour changes with the current investigation impossible.

In this current study and reviewed papers, significant colour changes were observed for pigmented elastomer specimens when stored in darkness. However, the addition of certain pigments improved the colour stability of the elastomer when compared with non-pigmented specimens. In the current study, addition of Indian Yellow and Alizarin Crimson to the base elastomer resulted in highest colour changes of 1.31 (W) and 1.24 (W), respectively, which was higher than the changes observed for the non-pigmented specimens with $\overline{\Delta E}$ values of 1.16 (W). All other pigments as well as a combination of pigments in a Caucasian skin tone resulted in lower colour changes than the non-pigmented specimens. Beatty *et al.* (1995) stated similar observations for Mars Violet and Yellow Ochre dry pigments, where the addition of these colourants lowered the overall colour changes below the PT of 1 ΔE and AT of 2 ΔE, respectively.

Non-pigmented platinum curing elastomer generally has a slightly yellow appearance and addition of colourants including red, green pigments as well as a combination of pigments found in a natural skin tone may have shifted the overall appearance of silicone elastomer to less yellow. Equally, adding of yellow pigments to the non-pigmented silicone may have increased the overall yellow appearance of specimens. However, evaluation of colour and colour changes within the three-dimensional L*a*b* colour space was not the focus of this study and needs to be investigated in future research.

3.4.2. Colour stability following accelerated ageing

3.4.2.1. Non-pigmented test specimens

It can be observed from the results of this part of the study that non-pigmented silicone elastomer specimens demonstrated colour changes ranging from 2.99 $\overline{\Delta E}$ (B) to 4.86 $\overline{\Delta E}$ (W) after 1500 hours of accelerated ageing. Based on the calculated $\overline{\Delta E}$, it can be stated that the AT of 2 ΔE was first crossed after 500 hours for samples assessed over the white background and after 700 hours for specimens assessed over the black background.

Beatty *et al.* (1995 and 1999) exposed non-pigmented A-2186 silicone elastomer (Factor II) to UVA and UVB light for a total of 1800 hours. They reported $\overline{\Delta E}$ of more than 7 for specimens exposed to UVA light and more than 8 for those exposed to UVB light. However, much smaller colour changes of approximately 2 ΔE were stated in their study from 1999 using a 70 : 30% weight ratio of 891 Type A adhesive (Dow Corning) and A-2186 (Factor II) and indicates that the made-up elastomer mix demonstrated better colour stability in the presence of UV-light.

Mancuso *et al.* (2009) investigated the colour stability of Silastic MDX 4-4210 (Dow Corning) and exposed test specimens to 1000 hours of accelerated ageing. The temperature of the weathering chamber was set at 60°C during the irradiation cycle and 40°C during the condensation/darkness cycle. No information was given on the irradiance strength of the light source used. The results showed $\overline{\Delta E}$ values of 0.16 at the end of the testing period; this is very low, clearly below the PT and different to the results found in the current study.

Hatamleh and Watts (2010 [a]) conditioned non-pigmented specimens made from TechSil S25 (Technovent) in a weathering chamber and exposed them to a xenon light source, providing 475 Wm^{-2} of total irradiance. The authors observed $\overline{\Delta E}$ values of 7.87 at the end of the testing phase of 360 hours which are significantly higher than the colour changes stated in the current study. At the equivalent time intervals of 300 and 400 hours in this current study, only small colour changes close to the PT of 1 ΔE were detected for specimens measured over both backgrounds.

The colour changes observed in this current study fall in between the minimum and maximum $\overline{\Delta E}$ values stated in the reviewed literature. However, a direct comparison of all studies is impossible due to varying research methodologies. All studies conclude significant colour changes of non-pigmented elastomer when exposed to accelerated ageing. These changes have been related to the damaging influence of UV-light that causes the silicone elastomer to degrade, affecting

colour stability as well as physical and mechanical properties (Beatty *et al.* 1995 and 1999; Hatamleh and Watts 2010 [a]; Mancuso 2009).

It has been suggested that UV-light induced photo oxidation of polymers may have resulted in formation of free radicals. A subsequent reaction of these radicals with oxygen could lead to formation of polymer oxy- and peroxy-radicals that would further lead to chain scission; and other free radicals may have reacted with each other resulting in cross-linking (Al-Harbi *et al*. 2015).

Beatty *et al.* (1995) stated that UV-light induced colour changes of non-pigmented elastomer may not be evident until a certain level/exposure of UV radiation is reached. This observation is in contrast with the current study as well as with the literature. Visible colour changes with $\overline{\Delta E}$ of 1.05 (B) and 1.35 (W) occurred already after 200 hours of accelerated ageing. The AT was crossed after 500 and 700 hours of conditioning with $\overline{\Delta E}$ of 2.65 (W) and 2.34 (B), respectively.

3.4.2.2. Pigmented test specimens

The organic pigment Logwood Maroon was the most colour stable colourant and demonstrated small colour changes with just crossing the PT at 1300 hours of accelerated ageing. The only investigated inorganic pigment, MeSi Green, exhibited good colour stability with maximum colour changes just crossing the PT ($\overline{\Delta E}$ of 1.21 (W) and 1.16 (B)). All remaining tested pigments as well as the combination of pigments in a Caucasian skin tone demonstrated clearly visible colour changes, also crossing the AT. Amongst all tested colourants, the organic pigment Indian Yellow was the least colour stable colourant with maximum $\overline{\Delta E}$ values of 5.2 (W) at the end of the testing period. These results support the known fact that inorganic pigments are generally more colour stable than organic pigments (Gary and Smith 1998).

Beatty *et al.* (1995) investigated the colour stability of five dry pigments when mixed into A-2186 (Factor) and exposed test specimens to UVA and UVB light. The authors stated high colour changes for the yellow pigment, Cadmium Yellow, with specimens exhibiting maximum $\overline{\Delta E}$ values between 16 (UVA light) and 25 (UVB light). However, specimens coloured with Cosmetic Yellow Ochre demonstrated much better colour stability with maximum $\overline{\Delta E}$ values ranging from 4 (UVA light) to 6 (UVB light). The colour changes observed for Cosmetic Yellow Ochre are similar to those observed for the least colour stable pigment in this current study, Indian Yellow.

The least colour stable pigment used in the study by Beatty *et al*. (1995) was Cosmetic Red with significant colour changes of more than 55 $\overline{\Delta E}$ when exposed to UVA and UVB light. This is in great contrast to the observations made for pigments utilised in this current study where the organic red pigment Logwood Maroon just crossed the PT and Alizarin Crimson exhibited maximum $\overline{\Delta E}$ of 2.5 (W) and 2.38 (B) after 1500 hours. However, a direct comparison of both studies is impossible due to the varying testing period, accelerated ageing setup and choice of colourants.

Beatty *et al.* (1995) stated that origin of pigments and the pigment composition were largely unknown as this is proprietary information of the manufacturers. The same situation applies for this current study and makes it impossible to draw conclusions about the colour stability of pigments based on their origin and chemical structure.

In a later study, Beatty *et al.* (1999) investigated the colour stability of oil-based pigments which included Cadmium Yellow, Yellow Ochre and a red pigment, namely Cadmium Red. The results showed improved colour stability for oil-based Cadmium Yellow with maximum colour changes ranging from 7 $\overline{\Delta E}$ (UVA light) to just above 9 $\overline{\Delta E}$ (UVB light). The colour changes observed for oil-based Yellow Ochre were higher (approximately 8 $\overline{\Delta E}$) than those detected for the dry pigment Cosmetic Yellow Ochre (4 to 6 $\overline{\Delta E}$) that was used in the earlier study by Beatty *et al.* (1995). Oil based Cadmium Red demonstrated colour changes of

approximately 8 $\overline{\Delta E}$ which represented significantly lower colour changes when compared with the dry Cosmetic Red. These results demonstrated improved colour stability of some oil-based pigments when mixed into silicone elastomer in comparison with the same dry pigment used as a colouring agent. However, all of these observed colour changes were considerably higher than those observed in the current study.

A series of investigations on the colour stability of pigmented silicone elastomer involving opacifiers at varying concentrations in combination with dry earth pigments, oil-based pigments and silicone pigments was performed by Kiat-Amnuay *et al*. (2002, 2006 and 2009). A direct comparison of these papers is impossible as different research methodologies were applied. However, it can be concluded that certain opacifiers at varying concentrations in combination with certain pigments resulted in either higher colour changes or in improved colour stability of pigmented silicone elastomer.

The use of red dry pigment in combination with 15% Georgia kaolin resulted in maximum $\overline{\Delta E}$ of 49.57, whereas the same pigment combined with 15% titanium white dry pigment as opacifier only demonstrated maximum $\overline{\Delta E}$ of 16.59. The application of silicone pigments achieved significantly less colour changes; maximum $\overline{\Delta E}$ were reported for the yellow pigment. All other pigment and opacifier combinations achieved maximum $\overline{\Delta E} < 2$. The colour changes observed for use of silicone pigments are similar to those in this current study and may be related to the similarity of colourants; in both studies colourants were dispersed in a silicone based pigment carrier.

Gary and Smith (1998) stated that inorganic pigments are more colour stable than organic pigments but application of the latter achieves more natural colouring results; they further concluded that organic pigments have a limited life span and are more subject to decay on ageing and exposure to adverse environmental conditions. The authors based their statements on the use of lightfastness categories, which reflect the level of resistance of pigments to fading, with pigments listed in category I being most colour stable. Three red and two yellow

pigments were discussed by the authors that had previously been used in facial prosthetics: Alizarin Crimson, an organic synthetic red pigment fell into the lightfastness category III, whereas Mars Violet and Cadmium-Barium Red, both inorganic synthetic pigments fell into category I. Cobalt Yellow and Yellow Ochre, both inorganic pigments, were listed in lightfastness category II and I, respectively.

Beatty *et al.* (1999) stated that oil-based pigments including titanium white, cadmium red, yellow ochre, cadmium yellow, mars violet (Grumbacher, Cransbury, NJ) demonstrated good colour stability in the uncombined state in the presence of UV radiation but showed significant colour changes when mixed into the silicone base elastomer. The authors postulated that either a chemical interaction or a chemical incompatibility between pigments and elastomer were responsible for the observed colour changes. With this knowledge in mind, the professional should consider the application of more light stable pigments in order to minimise colour changes of facial appliances.

A combination of pigments used in this current study to achieve a Caucasian skin tone resulted in higher $\overline{\Delta E}$ in comparison to application of pigments separately, but the observed colour changes were still lower than colour changes of pre-blended skin tones used in other studies (Al-Harbi *et al.* 2015; Hatamleh and Watts 2010 [a]). From the results of this study it is evidenced that colour changes in skin tone pigmented elastomer cannot be estimated from the colour changes known to occur in each of its component pigments.

3.4.3. Colour stability following natural outdoor weathering

3.4.3.1. Non-pigmented test specimens

The results showed that non-pigmented test specimens underwent significantly smaller colour changes when compared with the measurements recorded for artificial weathering. Non-pigmented silicone elastomer specimens

demonstrated $\overline{\Delta E}$ ranging from 2.42 (B) to 3.65 (W). This compares to higher colour changes of non-pigmented specimens after 1500 hours of accelerated ageing with maximum $\overline{\Delta E}$ values of 2.99 (B) and 4.86 (W).

Haug *et al*. (1999) performed colour stability testing of specimens made from Silastic MDX 4-4210 (Dow Corning) and A-2186 (Factor II) in Indiana, USA, where samples were exposed to outdoor weathering on the roof of the dental school for a period of six months. The authors recorded maximum colour changes of 3.52 $\overline{\Delta E}$ and 3.86 $\overline{\Delta E}$, respectively. Despite a different research methodology and no provided local weathering data during the testing period, these observed colour changes are similar to those obtained for non-pigmented M511 testing samples in this current study.

Polyzois *et al.* (1999) conducted a study on the colour stability of three non-pigmented maxillofacial silicones including Ideal (Orthomax, Bradford, UK), Silskin 2000 (De Puy Healthcare, Leeds, UK) and Elastosil M3500 (Wacker-Chemie GmbH, Munich, Germany) when exposed to natural outdoor weathering in Greece for one year. Lowest colour changes were observed for Elastosil and highest for Silskin, with $\overline{\Delta E}$ ranging from 2.13 to 3.98, respectively. The authors utilised a white calibration standard when recording colour measurements, which was the same method as used in this current study, and their measured values are similar to the recorded $\overline{\Delta E}$ values of 3.65 (W) in this current study. As the maximum temperatures and climate conditions were very different in Greece and the UK; it can be suggested that the elastomers tested by Polyzois *et al*. were more colour stable in the presence of UV-light than M511 tested in this current study.

Gary *et al.* (2001) investigated the colour stability of non-pigmented A-2186 (Factor II) when exposed to natural outdoor weathering in South Florida and Arizona from October 1998 until January 1999, providing a total sunlight exposure of 1305.7 MJm^{-2} and 1310.2 MJm^{-2}, respectively. The observed colour changes were higher in Arizona desert with 3.47 $\overline{\Delta E}$ when compared with South Florida demonstrating 1.11 $\overline{\Delta E}$, despite the recorded lower average temperatures

and rainfall. The colour changes for non-pigmented M511 in the current study are similar to those observed for Arizona desert. However, the minimum and maximum temperature in London during the testing period (4.6˚C and 15.5˚C, respectively) was significantly lower and the rainfall higher when compared to the weather data provided in the study by Gary *et al*. (2001).

Hatamleh and Watts (2010 [a]) exposed test specimens made from TechSil S25 (Technovent) to natural outdoor weathering on the roof of the Manchester Dental School for six months and observed colour changes of 3.89 $\overline{\Delta E}$. The authors obtained colour readings utilising a colorimeter in comparison to a spectrophotometer used in the current study. However, a white calibration standard was used when recording colour data in both studies. Despite a varying research methodology, the observed colour changes by Hatamleh and Watts are similar to those obtained for M511 testing specimens in this current study (3.65 $\overline{\Delta E}$) when measured over the white calibration background.

A recent study on the colour stability of maxillofacial silicone was performed by Al-Harbi *et al.* (2015) and included TechSil S25(Technovent), A-2186 and MED-4210 (Factor II). The authors exposed test specimens to outdoor weathering on the roof of the College of Dentistry at the University of Dammam, Saudi Arabia, for the duration of six months. Highest $\overline{\Delta E}$ were observed for non-pigmented TechSil S25 specimens (3.00 $\overline{\Delta E}$) and lowest for MED-4210 (2.58 $\overline{\Delta E}$). Despite much higher temperatures in Saudi Arabia, the authors stated a surprisingly better colour stability of TechSil S25 as it was reported by Hatamleh and Watts (2010 [a]), who conducted their study in the UK and suggests that beside temperature, humidity also has a significant effect on colour stability.
In comparison to the current study, it is interesting that all of the non-pigmented maxillofacial elastomers tested by Al-Harbi *et al*. demonstrated better colour stability than M511 specimens that were exposed to outdoor weathering in the UK. However, despite using a spectrophotometer for colour measurements in both studies, a different research methodology was applied which makes a direct comparison impossible.

3.4.3.2. Pigmented test specimens

All pigmented test specimens demonstrated significantly lower colour changes when compared with pigmented specimens exposed to accelerated ageing in a weathering chamber. Highest colour changes were observed for Alizarin Crimson coloured specimens with 1.48 $\overline{\Delta E}$ (W) and Caucasian skin with 1.26 $\overline{\Delta E}$ (W); lowest values were calculated for MeSi Green with 0.38 $\overline{\Delta E}$ (B). Interestingly, specimens coloured with Indian Yellow proved to be very colour stable with colour change values close to the PT of 1 ΔE.

Haug *et al*. (1999) investigated the colour stability of Silastic MDX 4-4210 (Dow Corning) and A-2186 (Factor II) when intrinsically coloured with five different colourants including dry earth pigments, rayon fibre flocking, artist's oil paints, kaolin (Factor II) and liquid facial cosmetic (Estée Lauder). Test samples were exposed to natural outdoor weathering on the roof of the Dental School at Indiana University for six months and from all tested colourants, rayon fibre flocking demonstrated highest colour changes with 4.59 and 4.60 $\overline{\Delta E}$, respectively. Lowest colour changes were observed for dry earth pigments with colour changes below 1 ΔE when used with A-2186 silicone elastomer. It is a known fact that inorganic pigments are very colour stable, and this is also reflected in the observed low colour changes for the inorganic pigment MeSi Green used in the current study.

In a later study, Gary *et al.* (2001) investigated the colour stability of A-2186 (Factor II) coloured with an inorganic pigment, Burnt Sienna, and two synthetic organic pigments, Hansa Yellow and Alizarin Red (Perma Colours) and exposed test specimens to natural outdoor weathering in two different locations, South Florida and Arizona desert, for a period of six months. The authors stated highest colour changes for Alizarin Red weathered in Arizona (9.33 $\overline{\Delta E}$) and lowest for Hansa Yellow (5.98 $\overline{\Delta E}$) tested in South Florida. The observed changes in colour are much higher than those observed by Haug *et al*. (1999) and those of the current study and may be related to the much warmer climate.

Hatamleh and Watts (2010 [a]) investigated the colour stability of TechSil S25 (Technovent) when intrinsically coloured with a pre-blended rose-pink skin shade (P409; Principality) and exposed test specimens to outdoor weathering on the roof of the Manchester Dental School for six months and stated $\overline{\Delta E}$ values of 8.30. Despite very similar weathering conditions and outdoor testing in the same climate, the observed colour changes are much higher than those calculated for M511 specimens in the current study, where maximum $\overline{\Delta E}$ values were stated for Alizarin Crimson with 1.48 $\overline{\Delta E}$ (W).

Al-Harbi *et al.* (2015) also conducted research on TechSil S25, as well as A-2186 and MED-4210 (Factor II). In both studies, test specimens had the same dimensions and were coloured with the same weight percentage of P409 (0.05 g for each 10 g of silicone elastomer) but Al-Harbi *et al.* calculated much lower colour changes of 4.31 $\overline{\Delta E}$. This is an interesting result as the research conducted by Al-Harbi *et al*. was carried out in a hot climate and higher colour changes would be expected due to the known negative effect of UV-light on pigments in terms of colour stability.

However, Al-Harbi *et al.* also investigated the colour stability of pigmented A-2186 and stated it underwent highest colour changes from all three tested silicone elastomers with $\overline{\Delta E}$ of 6.44. This result is still lower than the colour changes observed by Hatamleh and Watts (2010 [a]) for testing specimens in the British climate but are not too dissimilar from those stated by Gary *et al.* (2001) for samples tested in the South Florida climate. This indicates that similar climates/weather conditions may have a similar effect on the colour stability of pigments when mixed into maxillofacial silicone elastomer.

3.4.4. Influence of multifactorial environments

This study was limited to investigate the effect of darkness storage and UV radiation on the colour stability of maxillofacial non-pigmented and pigmented silicone elastomer within an artificial laboratory environment and when exposed to natural outdoor weathering. The weathering situations found during outdoor

exposure of test specimens could not be replicated in the artificial weathering chamber settings, where specimens were constantly exposed to artificial sunlight over a period of 1500 hours without different light intensities that are present during the course of a day as well as seasons being taken into consideration.

In order to better predict colour changes of facial prostheses in a service environment, other factors such as humidity, air pollution, body secretions, extrinsic colouring, personal habits of patients and naturally occurring colour changes of skin need to be evaluated.

Hatamleh and Watts (2010 [a]) investigated the effect of six different environmental factors on the colour stability of a maxillofacial silicone. However, as these environmental factors were investigated separately, no conclusion could be drawn for the material in a service environment. Ideally, research on the colour stability of maxillofacial elastomers should be carried out as in-vivo studies. Investigation of maxillofacial non-pigmented and pigmented elastomer in direct contact with human skin over a longer period of time will involve all environmental factors at the same time and only then the real effect of those can be assessed and a conclusion drawn on the prediction of colour stability of maxillofacial silicones in clinical service. This research approach would be most desirable but also most challenging to conduct.

3.4.5. Colour changes as a result of pigment changes or pigment movement

Beatty *et al.* (1999) stated that a series of pigments demonstrated good colour stability in the uncombined state in the presence of UV radiation but showed significant colour changes when incorporated into the base elastomer. The authors postulated that either a chemical interaction or a chemical incompatibility between pigments and elastomer were responsible for the observed colour changes.

The authors further investigated the effect of extrinsic colouring on the colour stability of pigmented maxillofacial silicone elastomer and stated that

incorporation of the same pigments into a surface sealant adhesive layer in higher concentration resulted in significant reductions in colour change, providing the sealant layer remained adherent.

However, it has generally been highlighted that pigments undergo varying degrees of colour changes when exposed to different environmental factors and that inorganic pigments are more colour stable than organic colourants (Gary and Smith 1998). Furthermore, it has been stated that pigments listed in the lowest lightfastness category I are most suitable to be used as they are less prone to undergo changes in colour when exposed to sunlight (Gary and Smith 1998). With this knowledge in mind the professional should choose most favourable colourants to be used when fabricating maxillofacial appliances.

The adverse effect of UV-light on the colour stability of pigments is generally known; however, another theory on the observed colour changes of maxillofacial silicone involves the movement of pigments within the elastomer. It has long been suggested that pigments may change their location within the elastomer over time as they are not chemically bonded to the elastomer. Hence, some of the colour changes observed in clinical service may be related to relocation of pigments, their movement towards the surface of the silicone elastomer and eventual loss of those pigments. However, currently this is a speculation and there is no scientific research available on this subject.

Based on a personal conversation with one of the most experienced maxillofacial technologists in the UK, pigment movement may be the possible result of colour changes. Some internal laboratory tests were carried out in the past where one half of a silicone elastomer sample was coloured with dry red pigments and exposed to UV-light on the window sill. Over a time period of approximately one year, the red pigments were more distributed and the previously clear side of the sample seemed slightly coloured until at some point the entire sample was found clear again. No scientific research was performed and this observation remained an internal laboratory test. However, it showed that pigments seemed to have

changed their location until the red pigments completely broke down chemically under the influence of UV-light.

Bellamy (2000) suggested that the extrinsic sealant layer acts as a mechanical barrier and its abrasion may allow pigment loss from the base elastomer which in turn results in deterioration of the colour stability of facial prostheses. This is an area that needs to be further explored, as it may show that pigments do not only change their colour but also move within the elastomer compound which could contribute to the observed overall colour changes. Currently, a PhD research project within this Department focusses on this subject and its results may hopefully help us to more understand the observed colour changes of maxillofacial elastomer and find solutions to minimise them.

Maxillofacial prosthetic rehabilitation has reached a high standard based on modern materials and techniques used in the fabrication of facial appliances. Today, their application improves greatly the quality of life of many patients afflicted with facial disfigurement. However, there is still room for improvement and substantiated knowledge of interactions between pigments, silicone elastomer and the intimate environment is required to find possible solutions in order to minimise colour changes of facial prostheses when used in clinical service.

3.5. Conclusion

From the results of this part of the study it can be concluded that storage in darkness resulted in smallest visible and exposure to accelerated ageing in a weathering chamber in highest visible colour changes of non-pigmented and pigmented M511 maxillofacial silicone elastomer. The colour changes of Caucasian skin coloured elastomer were different from the colour changes observed for some of the individual pigments that were used to establish this skin tone. However, the material combination of M511 silicone base elastomer and Spectromatch Pro colourants demonstrated good overall colour stability in this in-vitro study and can therefore be recommended for clinical use.

MEASUREMENT OF PHYSICAL AND MECHANICAL PROPERTIES

4.1. Introduction and aims of investigations

Today, PDMS elastomers are most frequently used when manufacturing facial prostheses. However, they have been described as far from ideal in terms of their colour stability and physical and mechanical properties (Aziz *et al.* 2003; Bellamy *et al.* 2003).

Adequate tear strength, tensile strength and hardness are amongst the essential properties a silicone elastomer should possess and are a measure of overall strength and flexibility of silicone elastomers and consequently of facial prostheses (Chalian and Philips 1974; Conroy *et al.* 1979; Roberts 1971). Today, a large variety of maxillofacial elastomers have become available and research has been conducted to investigate the physical and mechanical properties of silicones in order to recommend their use for maxillofacial prosthetic applications (Aziz *et al.* 2003; Eleni *et al.* 2011; Hatamleh and Watts 2010[b]; Polyzois *et al.* 1994).

Individual colouring of elastomer is required when constructing facial prostheses and various colourants including dry pigments, oil based pigments as well as silicone based pigments have been used by clinicians; however, only few investigations have been conducted on the effects of colourants on the physical and mechanical properties of silicone elastomer (Al-Harbi *et al.* 2015; Haug *et al.* 1999; Tram Nguyen *et al*. 2013).

More research has been conducted on how environmental factors may influence the physical and mechanical properties of maxillofacial elastomer and involved the use of accelerated ageing, natural outdoor weathering as well as storage in darkness. It was shown that elastomers were affected at varying degrees which was depended upon both, the elastomer and environment (Al-Harbi *et al.* 2015;

Dootz *et al.* 1994; Haug *et al.* 1999; Kheur *et al.* 2012; Polyzois and Andreopoulos 1993; Willett and Beatty 2015).

However, limited research has been conducted on the physical and mechanical properties of M511 silicone elastomer and no investigations have been performed in conjunction with the Spectromatch Pro colouring system. The aims and objectives of this part of the study involved investigations on the effects of various environmental conditions on tear strength, tensile strength and hardness of non-pigmented and pigmented M511 elastomer.

4.2. Materials

The materials used in this part of the study are the same as previously used in Chapter 3, section 3.2.

4.3. Study design

Seven test groups were designed and included non-pigmented M511, elastomer coloured with Alizarin Crimson, Logwood Maroon, Indian Yellow, MeSi Green, Malachite Green and a combination of pigments to establish a Caucasian skin tone. Six samples of each test group and per testing method (tensile, tear and hardness testing) were exposed to a) storage in darkness, b) accelerated ageing and c) natural outdoor weathering. Furthermore, d) non-weathered specimens served as a Control and were tested directly following their manufacture. A total of 168 silicone specimens were investigated per testing method (Fig. 4.1) and sample size was based on previous studies (Dootz *et al*. 1994; Haug *et al*. 1992; Polyzois *et al*. 2000; Willett and Beatty 2015).

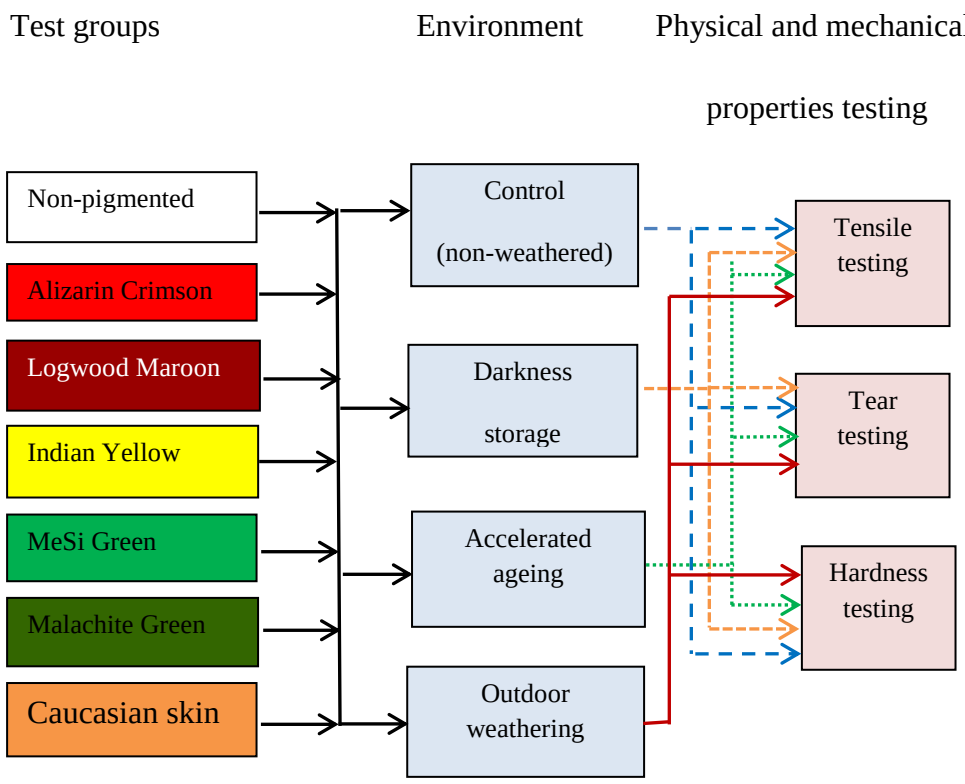


Fig. 4.1: Study design.

4.4. Methods

4.4.1. Preparation of test specimens

4.4.1.1. Tensile test specimens

For manufacture of tensile test specimens, silicone elastomer and pigments were weighed and mixed as described in Chapter 3, section 3.2.1. A PTFE lined aluminium mould was used for fabrication of dumbbell shaped tensile test specimens (Fig. 4.2). Samples were manufactured in accordance to BS 903 Part A2 (1995).

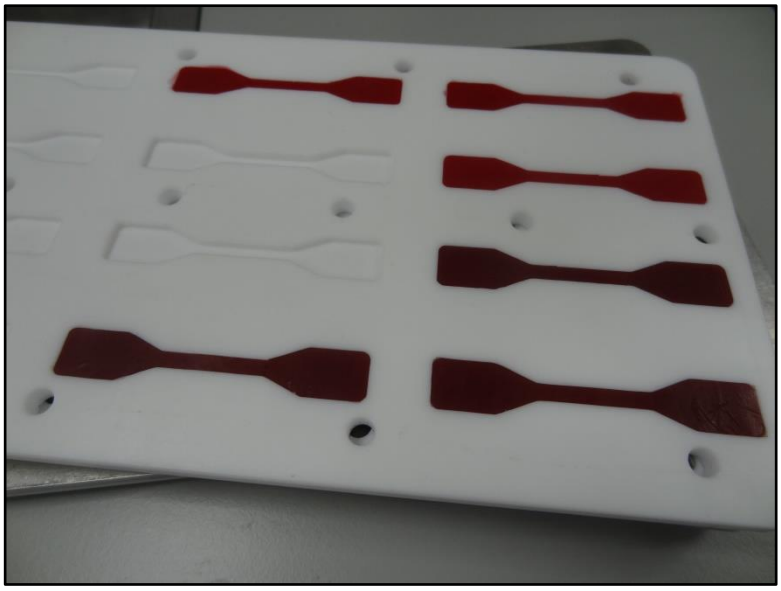


Fig. 4.2: PTFE lined mould for fabrication of dumbbell shaped tensile test specimens.

4.4.1.2. Tear test specimens

For manufacture of tear test specimens, silicone elastomer and pigments were weighed and mixed as described in Chapter 3, section 3.2.1. The material was then processed utilising an aluminium mould with PTFE inserts for fabrication of tear test specimens. Samples were manufactured in accordance to BS 903 Part A3 (1995). Initial tear tests demonstrated slip-stick behaviour of M511; test samples underwent initial tearing, followed by a resistance to tearing for a time, and then continued tearing to break. Therefore, samples were modified utilising specimens with 50 mm length and an introduced cut of 10 mm length which was similar to alterations applied in other studies when observing slip-stick behaviour of maxillofacial elastomer during tear testing (Aziz *et al.* 2003; Bellamy *et al.* 2003).

4.4.1.3. Hardness test specimens

For the purpose of hardness testing, test specimens were prepared as described in Chapter 3, section 3.2.1 and was in accordance to ASTM D2240 (ASTM 2003).

4.4.2. Weathering of test specimens

Specimens were stored in darkness, exposed to accelerated ageing and natural outdoor weathering as described in Chapter 3, section 3.2.2.

4.4.3. Specimen conditioning

Prior to physical and mechanical properties testing, specimens were cleaned with a mild detergent (Procter & Gamble) and distilled water in order to remove any surface grime. They were then wiped dry and conditioned in order to adjust to the laboratory room temperature where mechanical testing was performed. Samples were conditioned for 24 hours at room temperature which was maintained at 21 ± 2°C in order to minimise the effects of temperature on the results of physical and mechanical properties testing.

4.4.4. Physical and mechanical properties testing procedures

4.4.4.1. Tensile strength

The specimens were tested in accordance to BS 903 Part A2 (1995). The test was carried out utilising the Instron 5569A testing machine (Instron, High Wycombe, UK) which was fitted with a 500 N load cell. Specimens were positioned between the sample grips of the Instron with a distance between them maintained at 45 mm; specimens were pulled apart to failure at a constant cross head speed of 50 mm min^{-1}. Tensile strength (MPa) and percent elongation (%) were automatically calculated by the Instron Bluehill software (version 2.21; Instron).

4.4.4.2. Tear strength

Tear strength testing was performed in accordance to BS 903 Part A3 utilising the Instron 5569A testing machine. The device was fitted with a 500 N load cell and specimens were tested at a constant cross head speed of 100 mm min^{-1} at a gauge length of 10 mm (maintained distance between sample grips). On failure of test specimens, the Instron Bluehill software automatically calculated the tear strength (N mm^{-1}).

4.4.4.3. Hardness testing

The hardness test utilised in this study was based on measurements of the indentation of a metal pin into the test specimen under specified conditions and conducted according to ASTM D2240 (ASTM 2003). A Sauter hardness tester (TI-A0; Sauter GmbH, Balingen, Germany) was used with the results being directly obtained in Shore A hardness.

4.5. Statistical analysis

The statistical analysis of the data of this part of the study was the same as previously described in Chapter 3, section 3.2.4.

4.6. Results

All recorded data for physical and mechanical properties testing is provided in Appendix E and stored on the CD which is enclosed with this thesis.

4.6.1. Tensile strength

There was a statistically significant effect of all pigments, environments, pigment and environment interactions on tensile strength and percent elongation for non-pigmented and pigmented M511 elastomer ($p = 0.001$). A univariate summary of data is provided in Tables 4.1 and 4.2.

Tensile strength (MPa)				
Test group	Environments			
	Control Mean, sd	Darkness Mean, sd	Accelerated Mean, sd	Outdoor Mean, sd
Non-pigmented	2.99, 0.18	3.30, 0.75	4.63, 0.71	4.93, 0.39
Alizarin Crimson	3.67, 0.16	3.23, 0.33	4.08, 0.52	3.92, 0.74
Logwood Maroon	3.49, 0.44	3.35, 0.40	4.49, 0.78	4.29, 0.34
Indian Yellow	3.09, 0.84	2.95, 0.41	3.72, 0.86	4.55, 0.64
Malachite Green	3.19, 0.63	2.90, 0.27	3.83, 0.71	4.20, 0.41
MeSi Green	3.44, 0.45	2.83, 0.50	4.50, 0.73	4.51, 0.33
Caucasian skin	3.17, 0.51	3.31, 0.60	4.14, 0.39	5.26, 0.61

Table 4.1: Univariate summary statistics of tensile strength data for pigments and environments.

Percent elongation (%)				
Test group	Environments			
	Control Mean, sd	Darkness Mean, sd	Accelerated Mean, sd	Outdoor Mean, sd
Non-pigmented	488.36, 21.52	352.54, 64.08	315.44, 39.51	382.29, 19.99
Alizarin Crimson	467.56, 9.85	367.23, 38.18	324.89, 27.89	371.81, 58.32
Logwood Maroon	447.72, 42.48	373.03, 31.82	325.24, 38.04	371.55, 17.04
Indian Yellow	312.49, 70.91	371.43, 36.00	319.94, 51.79	396.98, 40.78
Malachite Green	330.01, 52.64	318.89, 29.55	281.98, 41.47	351.11, 25.37
MeSi Green	363.08, 31.93	336.79, 41.70	317.29, 39.06	359.01, 22.80
Caucasian skin	345.61, 42.37	392.78, 48.77	305.93, 25.46	434.32, 46.82

Table 4.2: Univariate summary statistics of percent elongation data for pigments and environments.

Comparison of pigments and environments for tensile strength and percent elongation was carried out applying Šídák's multiple comparisons test (Table 4.3).

		Tensile strength	Percent Elongation
Environments	Darkness	A	
	Accelerated ageing		
	Outdoor		A
	Control	A	A
Pigments	Non-pigmented	A	D
	Alizarin Crimson	A	D
	Logwood Maroon	A	C D
	Indian Yellow	A	A B C
	Malachite Green	A	A
	MeSi Green	A	A B
	Caucasian skin	A	B C D

Table 4.3: Šídák's multiple comparison of tensile strength and percent elongation for each environment and pigment.

Environments and pigments sharing the same letter are not statistically significantly different.

Accelerated ageing and outdoor weathering had a greater effect on tensile strength than darkness. Tensile strength increased for weathered non-pigmented samples and ranged from 3.30 MPa (darkness) to 4.93 MPa (outdoor) when compared with the Control group (2.99 MPa); however, percent elongation decreased for weathered non-pigmented samples and ranged from 315.44% (accelerated ageing) to 382.29% (outdoor weathering) in comparison to the Control group (488.36%).

Adding of pigments increased the tensile strength and ranged from 3.09 MPa (Indian Yellow) to 3.67 MPa (Alizarin Crimson) when compared with non-pigmented (2.99 MPa) but decreased percent elongation ranging from 312.49% (Indian Yellow) to 467.56% (Alizarin Crimson) in comparison with non-pigmented elastomer (488.36%).

The mean values for tensile strength and percent elongation and associated 95% confidence intervals for all pigments and environments are illustrated in Figs. 4.3 and 4.4.

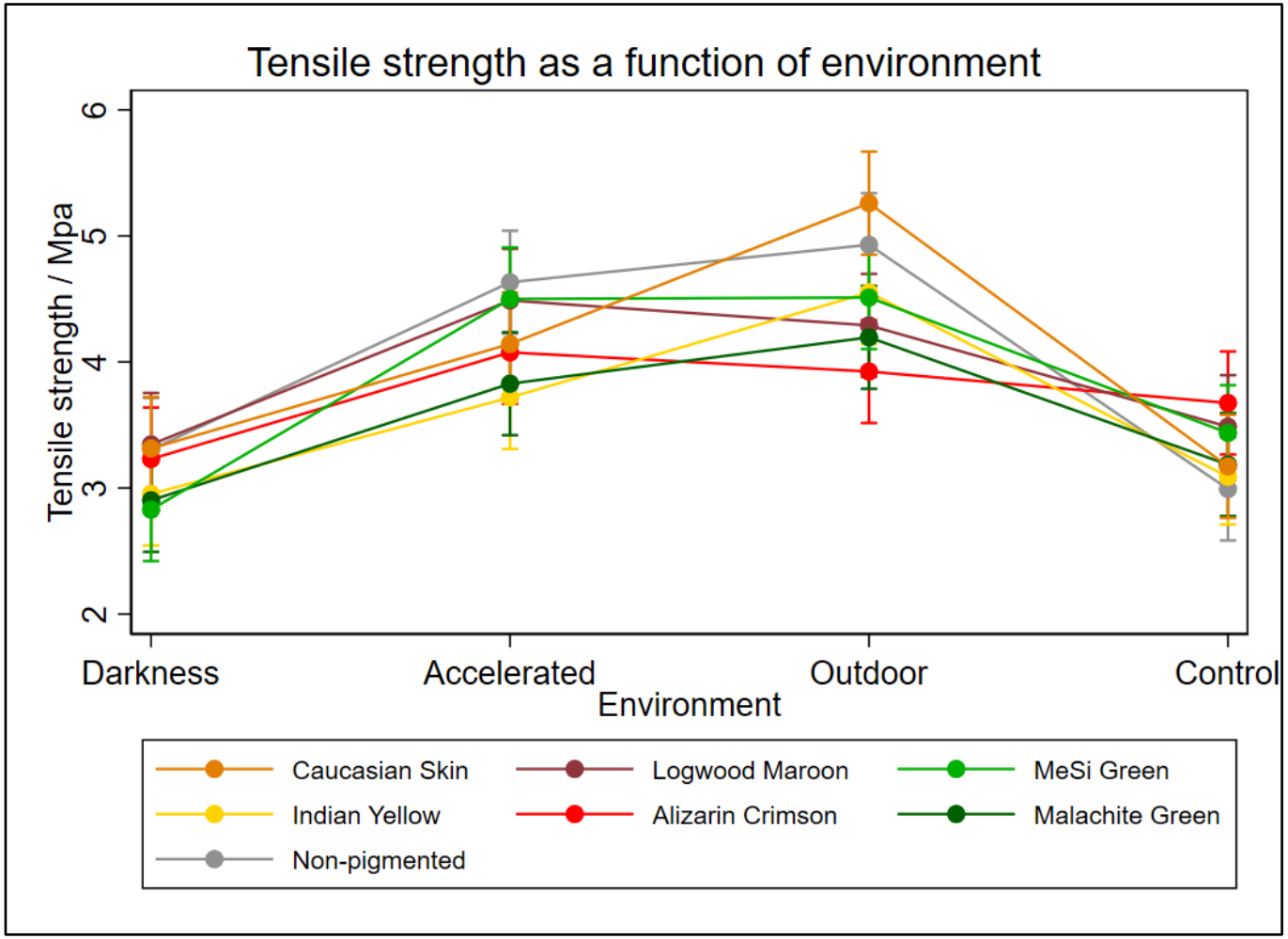


Fig. 4.3: Average tensile strength and associated 95% confidence interval.

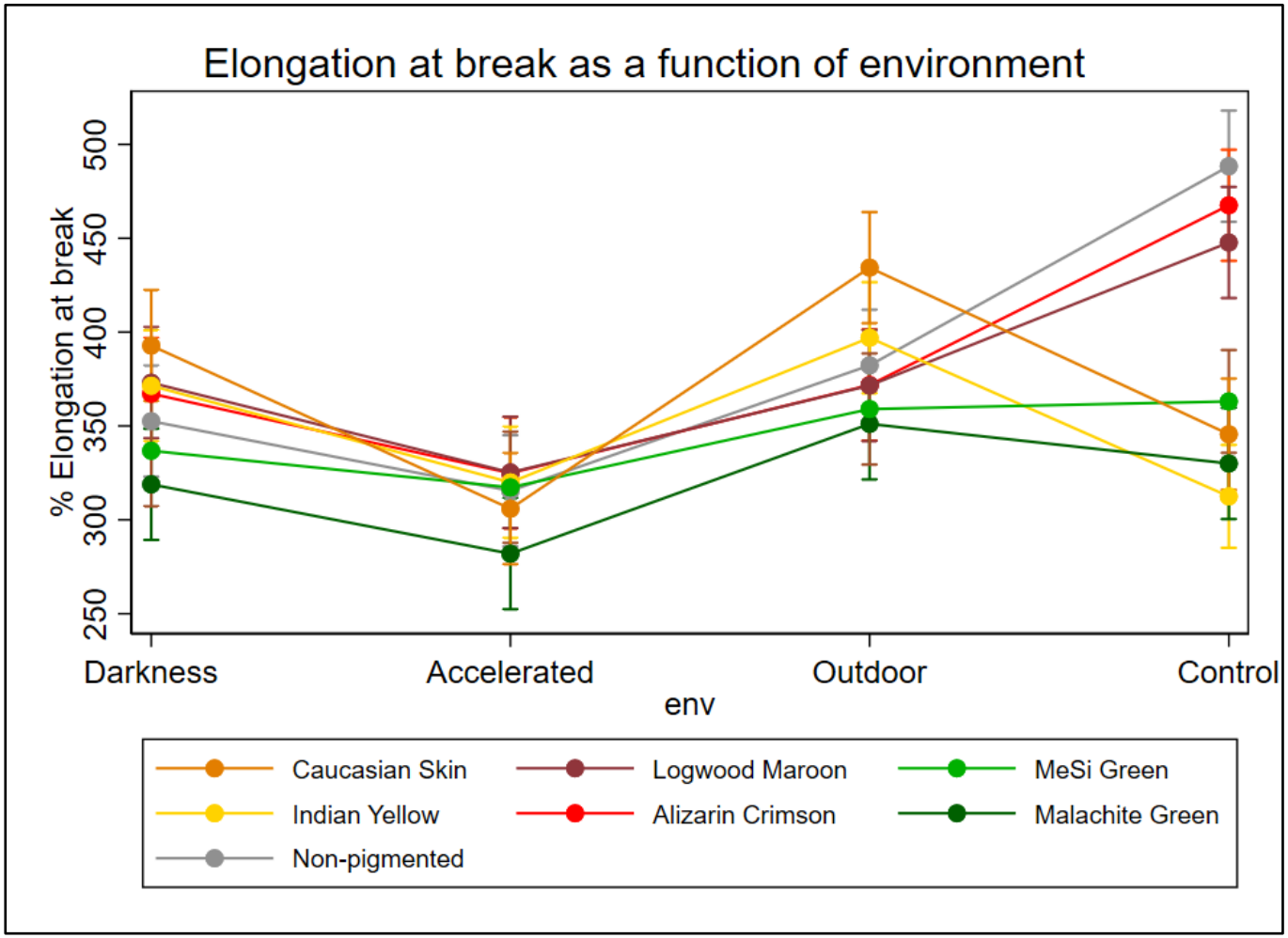


Fig. 4.4: Average percent elongation and associated 95% confidence interval.

4.6.2. Tear strength

There was no statistically significant effect for all pigments, environments, pigment and environment combinations on the tear strength of non-pigmented and pigmented M511 elastomer. However, there was a statistically significant effect of environment ($p = 0.001$) with the Control group (non-weathered samples) being significantly different from the other environments which are not statistically significantly different from each other. A univariate summary of data is provided in Table 4.4.

Tear strength (N mm^{-1})				
Test group	Control Mean, sd	Darkness Mean, sd	Accelerated Mean, sd	Outdoor Mean, sd
Non-pigmented	4.18, 0.43	4.51, 1.17	4.81, 0.41	4.62, 0.53
Alizarin Crimson	4.92, 0.87	4.43, 1.32	4.40, 0.59	4.72, 0.50
Logwood Maroon	4.48, 0.46	4.63, 0.87	4.84, 0.84	4.43, 1.05
Indian Yellow	5.07, 0.34	4.41, 0.71	4.80, 0.63	4.38, 0.98
Malachite Green	5.08, 0.42	4.61, 1.00	4.42, 0.66	4.08, 0.57
MeSi Green	5.46, 0.18	4.44. 0.47	4.65, 0.87	4.70, 0.90
Caucasian skin	5.16, 0.42	4.37, 1.03	4.74, 0.51	4.90, 0.65

Table 4.4: Univariate summary statistics of tear strength data for all pigments and environments.

For Control samples, the lowest tear strength was measured for non-pigmented specimens with 4.18 N mm^{-1}; highest tear strength of all test samples was measured for MeSi Green Control with 5.46 N mm^{-1} and lowest for Malachite Green outdoor with 4.08 N mm^{-1}.

The mean values for tear strength for all data, all environments, pigments, and environment and pigment combinations are illustrated in Figs. 4.5 and 4.6.

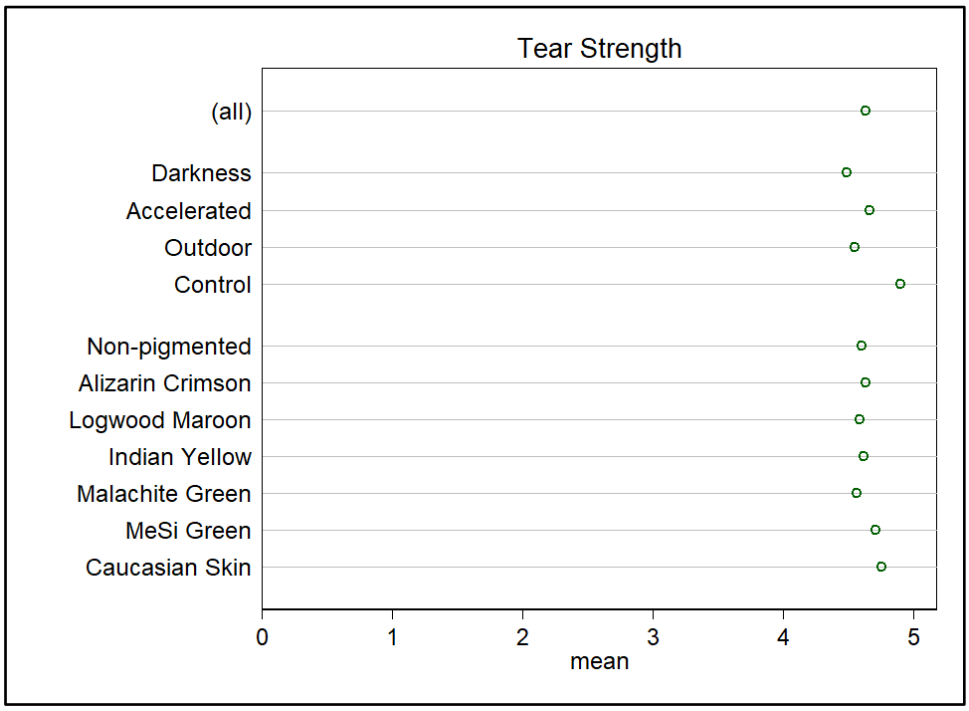


Fig. 4.5: Mean tear strength (N mm^{-1}) for all data, all environments and all pigments.

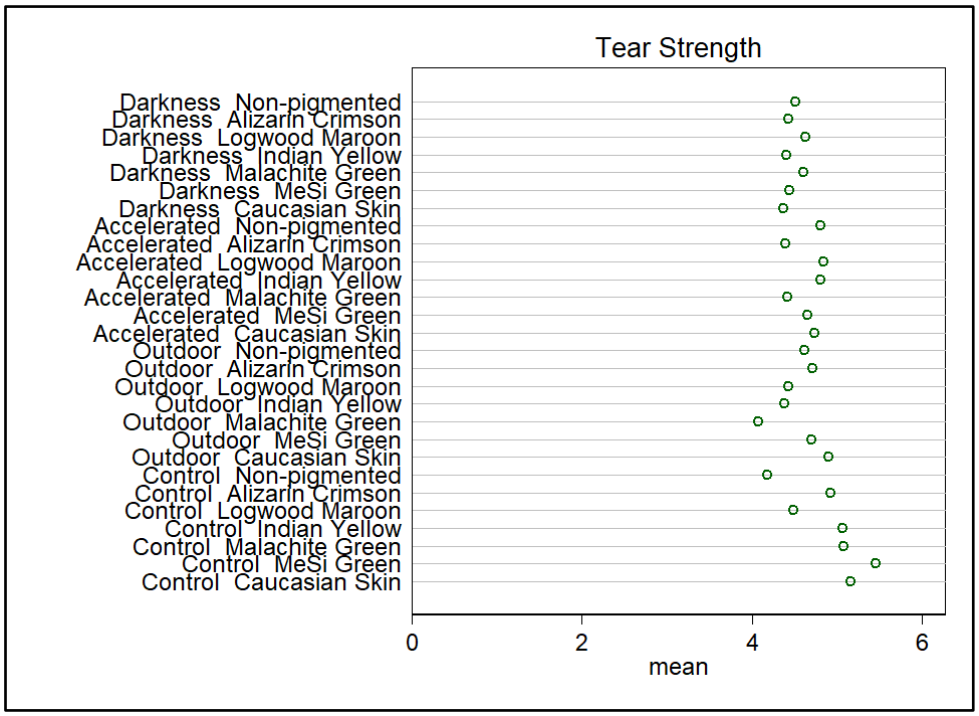


Fig. 4.6: Mean tear strength (N mm^{-1}) for all environment and pigment combinations.

4.6.3. Hardness testing

There was a statistically significant effect of pigments, environments, time and their interactions on the hardness of non-pigmented and pigmented M511 elastomer ($p = 0.001$). A univariate summary of data is provided in Table 4.5.

Test group		Accelerated		Darkness		Outdoor	
		Time/h		Time/h		Time/h	
		0	1500	0	1500	0	1500
Non-pigmented	Mean	24.92	35.51	25.01	26.86	25.11	32.76
	SD	0.42	0.58	0.66	0.59	0.24	0.65
Indian Yellow	Mean	24.39	31.33	23.46	24.97	23.81	31.67
	SD	0.40	0.77	0.42	0.57	0.30	0.48
Alizarin Crimson	Mean	24.08	31.60	24.75	27.00	24.17	29.97
	SD	0.30	0.62	0.30	0.27	0.46	0.52
Logwood Maroon	Mean	23.86	33.21	24.42	26.79	23.83	32.08
	SD	0.47	0.48	0.41	0.45	0.32	0.46
Malachite Green	Mean	24.72	32.25	24.71	26.99	24.79	32.19
	SD	0.28	0.92	0.45	0.54	0.37	0.40
MeSi Green	Mean	24.46	32.14	24.54	26.13	24.43	32.22
	SD	0.37	0.88	0.40	0.58	0.38	0.40
Caucasian skin	Mean	23.94	31.13	24.68	25.71	23.76	31.64
	SD	0.37	0.79	0.38	0.53	0.41	0.65

Table 4.5: Univariate summary statistics of hardness testing data for all pigments and environments at 0 and 1500 hours.

Non-pigmented Control samples demonstrated hardness values from 24.92 to 25.11 Shore-A. Adding of pigments decreased the hardness of all pigmented Control samples, highest values were measured for Malachite Green with 24.79 Shore-A and lowest for Indian Yellow with 23.46 Shore-A. All three environments increased the hardness for all test samples, with accelerated ageing and outdoor weathering having a greater effect than darkness. Highest hardness values of all samples were measured for non-pigmented specimens exposed to accelerated ageing with 35.51 Shore-A and lowest for Indian Yellow stored in darkness with 24.97 Shore-A.

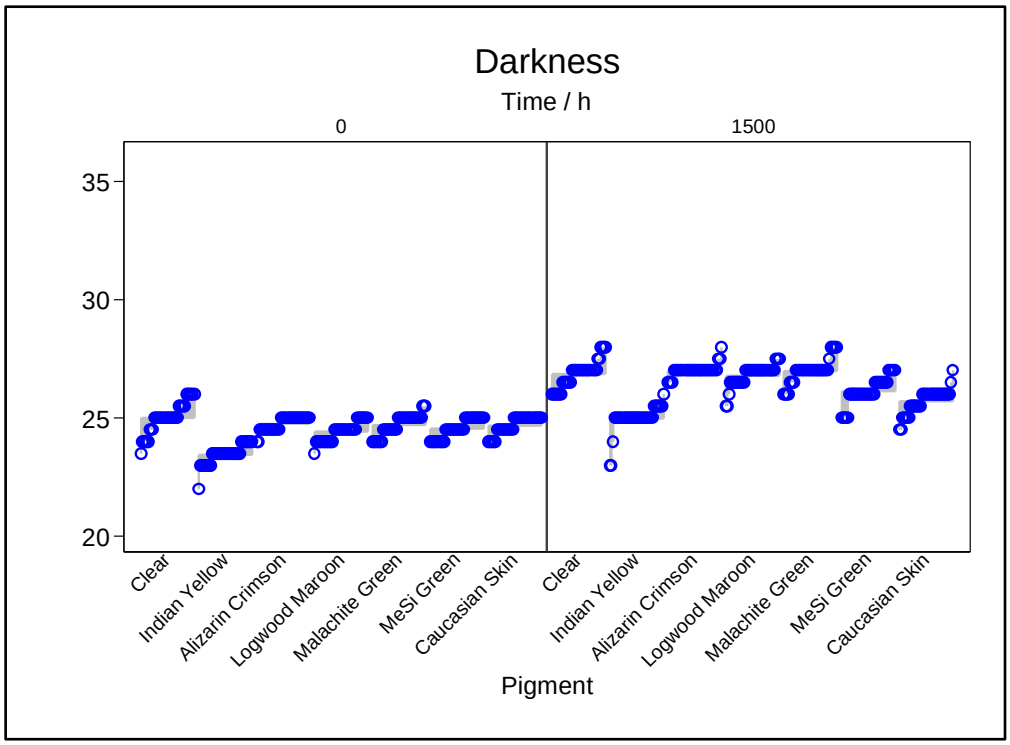
Comparison of pigments and environments for hardness was performed applying Šídák's multiple comparisons test (Table 4.6).

	Pigment	Šidák
Darkness	Caucasian skin	A
	Logwood Maroon	B
	Indian Yellow	
	Alizarin Crimson	C
	Me Si Green	A
	Non-pigmented	C
	Malachite Green	BC
Outdoor Weathering	Caucasian skin	A
	Logwood Maroon	B
	Indian Yellow	AB
	Alizarin Crimson	
	Me Si Green	C
	Non-pigmented	
	Malachite Green	C
Accelerated Ageing	Caucasian skin	
	Logwood Maroon	B
	Indian Yellow	A
	Alizarin Crimson	A
	Me Si Green	B
	Non-pigmented	
	Malachite Green	B

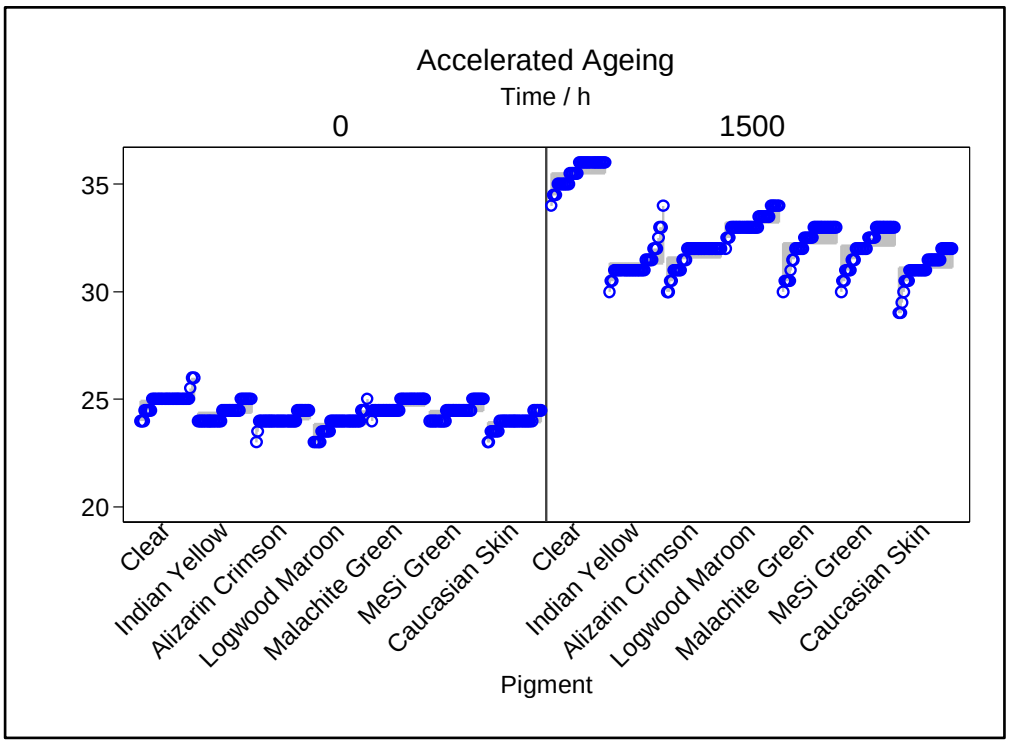
Table 4.6: Šídák's multiple comparison of hardness for each pigment environment combination.

Pigments sharing the same letter are not statistically significantly different.

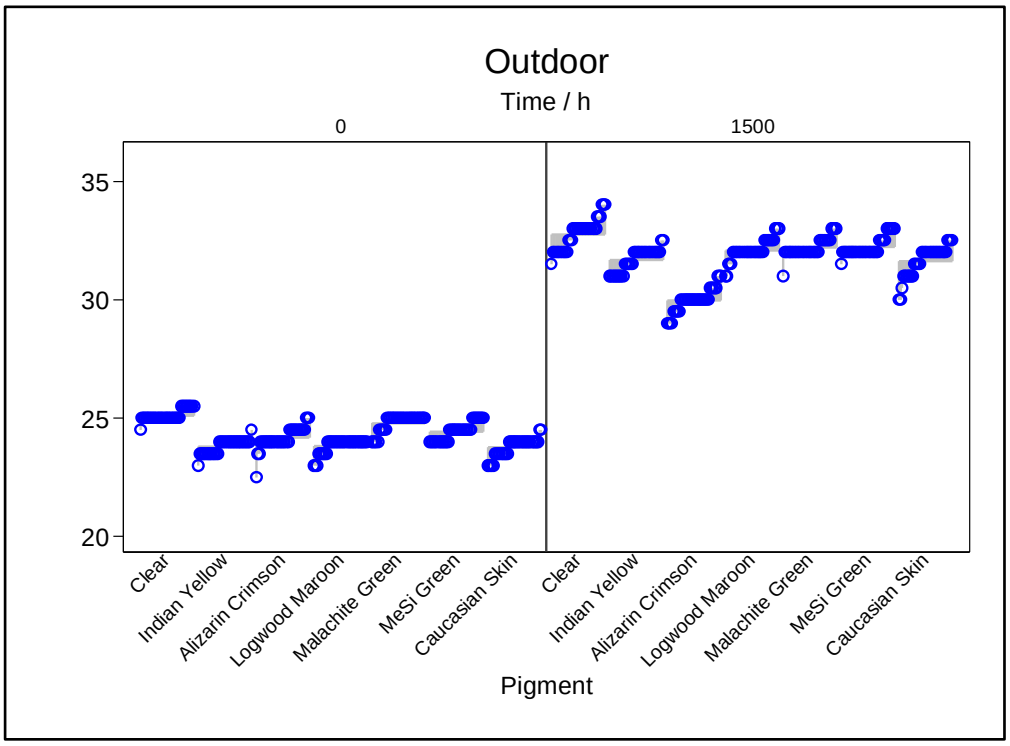
The mean values for hardness and deviations from the means for all pigments and environments at baseline (0 hours) which served as a Control group and 1500 hours are illustrated in Figs. 4.7 a, b and c.


Darkness
Time / h
0
1500
35
30
25
20
Clear
Indian Yellow
Alizarin Crimson
Logwood Maroon
Malachite Green
MeSi Green
Caucasian Skin
Pigment

(a)


Accelerated Ageing
Time / h
0
1500
35
30
25
20
Clear
Indian Yellow
Alizarin Crimson
Logwood Maroon
Malachite Green
MeSi Green
Caucasian Skin
Pigment

(b)



(c)

Fig. 4.7: Deviation plots for Hardness (Shore-A) at 0 and 1500 hours for (a) darkness, (b) accelerated ageing and (c) outdoor weathering.

The plots show the deviation of each data point from in the mean value in ascending order.

4.7. Discussion

This part of the study was designed to investigate tensile strength, tear strength and hardness of non-pigmented and pigmented M511 test specimens when exposed to different environments; and the results showed that the physical and mechanical properties of the elastomer were affected by storage in darkness, accelerated ageing and outdoor weathering. Accordingly, we reject the null hypothesis. However, the environmental conditions did not have a statistically significant effect on the tear strength of M511 elastomer and we fail to reject the null hypothesis for this part of investigations.

It has been stated that the mechanical properties of silicone elastomers are governed by their chemical structure involving molecular weight distribution, the selection of filler and cross-linking of polymer chains to establish a polymer network; and optimum balance of the above will result in silicone elastomers that are suitable for maxillofacial prosthetic applications (Aziz *et al*. 2003; Bellamy *et al.* 2003).

Sweeney *et al.* (1972) were the first to publish, and Conroy *et al.* (1979) and Lewis and Castleberry (1980) later updated data describing desired values for physical and mechanical properties of a maxillofacial elastomeric material. Over the last four decades, numerous research projects showed varying data of physical and mechanical properties of popular maxillofacial elastomers. However, the measured properties of those tested elastomers including tear strength, tensile strength and hardness were within range of the recommended values and hence most of those materials are still used when constructing facial prostheses (Hatamleh and Watts 2010[b]; Lai *et al.* 2002; Moore *et al*. 1977; Kouyoumdjian *et al*. 1985; Polyzois *et al.* 1994).

4.7.1. Physical and mechanical properties of non-weathered samples

The results of this part of the study showed that tensile strength and tear strength increased whereas percent elongation and hardness decreased when comparing

non-pigmented and pigmented M511 elastomer. Tear and tensile strength are a measure to express the overall strength of elastomer and was improved with addition of pigments to the elastomer; however, its flexibility was adversely affected at the same time and would in particular influence the fine prosthesis margins.

Tensile strength and tear strength were lowest for non-pigmented M511 with 2.99 MPa and 4.18 N mm^{-1}, respectively, but increased when adding pigments to the silicone elastomer. Highest tensile strength of all pigmented silicone specimens was obtained for Alizarin Crimson coloured elastomer with 3.67 MPa and lowest for Indian Yellow with 3.09 MPa, whereas highest tear strength was measured for MeSi Green with 5.46 N mm^{-1} and lowest for Logwood Maroon with 4.48 N mm^{-1}.

Percent elongation was highest for non-pigmented specimens with 488.36% and decreased when adding pigments. Highest values were measured for Alizarin Crimson with 467.56% and lowest for Indian Yellow with 312.49%. Non-pigmented specimens demonstrated highest hardness values with 25.11 Shore A. Hardness generally decreased when adding pigments to the base elastomer and was lowest for Indian Yellow with 23.46 Shore A. Highest hardness values of pigmented specimens were measured for Malachite Green with 24.79 Shore A.

Spectromatch Pro colourants were used in this study where pigments are dispersed in a mix of M511 base elastomer, silicone oil and functional fluid. Addition of pigments during the colouring process resulted in an altered base elastomer and cross-linker ratio, and together with the presence of silicone oil and functional fluid these may have led to an altered polymer network which in turn affected the physical and mechanical properties of the material.

Hardness decreased with incorporation of pigments and may be related to the pigment carrier. The utilised pigment paste consisted of pigments that were added to a mix of M511 base elastomer, silicone oil and functional fluid; and silicone oil may have acted as a plasticiser and thereby lowered elastomer hardness.

However, the exact composition of the pigment carrier is proprietary and was not fully disclosed by Spectromatch Ltd.

Limited research was conducted on the physical and mechanical properties of pigmented elastomers. Abdelnnabi *et al.* (1984), Haug *et al.* (1999) and Tram Nguyen *et al*. (2013) investigated the tensile strength, percent elongation, tear strength and hardness of non-pigmented and pigmented MDX-4-4210 (Dow Corning). Abdelnnabi *et al.* (1984) did not provide any information on the colourants used in their study but stated that the measured physical and mechanical properties of non-pigmented when compared with pigmented MDX-4-4210 were not statistically significantly different. This is in contrast to the current study where only tear strength was not affected by the application of silicone-based pigments and may be related to the use of a different elastomer, colourants and research methodology.

Haug *et al.* (1999) compared non-pigmented MDX-4-4210 with pigmented elastomer when coloured with dry earth pigments, artists' oil paints, rayon flocking (Factor II) and liquid cosmetic (Estée Lauder). The authors found no statistically significant effect on tensile strength and tear strength when adding colourants to MDX-4-4210. However, addition of artists' oil paints significantly increased the percent elongation by 24% when comparing non-pigmented with pigmented elastomer. The oil used as a colourant medium may have acted as a plasticiser resulting in a more flexible material. However, addition of flocking had the opposite effect and significantly decreased percent elongation by 20%; it may be explained that incorporation of these particles into the elastomer resulted in a less flexible material.

There was no statistically significant effect on the hardness of MDX-4-4210 when adding dry earth pigments but adding artists' oil paints or liquid cosmetic resulted in a significant decrease by approximately 7%. Nevertheless, addition of kaolin and rayon flocking had the opposite effect with resulting in a significant increase of hardness by approximately 19% where these incorporated particles caused the material getting harder. The use of silicone-based pigments in this

current research altered the above listed mechanical properties of M511 silicone; however, a direct comparison of both studies was not possible due to varying materials and methodology.

Tram Nguyen *et al*. (2013) added 10% of different opacifiers including titanium white dry pigment, silicone intrinsic white (Factor II) and UV mineral-based light protecting agent (LP; Colore Science) to MDX-4-4210 in combination with two colourant systems. The authors stated that only the application of the three different opacifiers had a significant effect on the physical and mechanical properties of MDX-4-4210 ($p < 0.001$). The use of silicone white as opacifier resulted in increased tear strength, tensile strength, percent elongation at break and decreased hardness and was similar to the observations made in this current study; this may be related to similarity with regards to applied silicone based colourants.

4.7.2. Effects of environments on physical and mechanical properties

It can be stated that environment had a statistically significant effect on tensile strength, percent elongation and hardness of non-pigmented and pigmented M511 silicone elastomer ($p = 0.001$). There was no statistically significant effect of environment on the tear strength of test specimens; however, Control samples (non-weathered test specimens) were statistically significantly different from all environments ($p = 0.001$).

In this current study, tensile strength was higher following accelerated ageing and outdoor weathering than after darkness storage for all test groups. Lowest tensile strength was observed for MeSi Green after darkness storage with 2.83 MPa and highest for Caucasian skin following outdoor weathering with 5.26 MPa. Percent elongation was lowest for all non-pigmented and pigmented specimens following accelerated ageing. Lowest values were measured for Malachite Green after accelerated ageing with 281.98% and highest for Caucasian skin after outdoor weathering with 434.33%.

No effect was observed for any of the tested environments on the tear strength of M511. However, for most test groups accelerated ageing and outdoor weathering resulted in higher tear strength than following darkness storage. Lowest and highest tear strength was recorded following outdoor weathering for Malachite Green and Caucasian skin with 4.08 and 4.90 N mm^{-1}, respectively.

Hardness increased for all test specimens and environments. However, accelerated ageing most affected the hardness of non-pigmented M511 elastomer with 35.51 Shore A followed by 33.21 Shore A for Logwood Maroon coloured specimens. Lowest values of 24.97 Shore A were obtained for Indian Yellow following darkness storage.

Accelerated ageing and outdoor weathering both involve the influence of UV light. Eleni *et al*. (2009) stated that in irradiated polymers both, cross-linking and chain scission occur. The observed changes in this current study involved increased tensile strength and reduced percent elongation after accelerated ageing and outdoor weathering, where the effect of UV-light may have resulted in increased cross-linking and a higher density of the polymer network which in turn improved the resistance to failure during material stretching but consequently reduced the overall ability to stretch due to a tighter polymer network.

A decrease of tensile strength was observed for all specimens apart from non-pigmented and Caucasian skin following darkness storage which suggests that with time and without the effect of UV-light chain scission was the main chemical reaction taking place and resulting in detachment of densely cross-linked regions within the polymer network (Aziz *et al*. 2003; Bellamy *et al*. 2003; Eleni *et al*. 2009 and 2011; Willett and Beatty 2015).

Tear strength increased for non-pigmented specimens when weathered in all environments and suggests that cross-linking was the main chemical reaction taking place (Aziz *et al*. 2003; Bellamy *et al*. 2003; Eleni *et al*. 2009 and 2011; Willett and Beatty 2015). However, addition of pigments decreased tear strength for all pigmented specimens apart from Logwood Maroon; incorporated silicone

oil and functional fluid in the pigment paste may have affected the structure and density of the polymer network and thereby reduced the materials' tear strength (Aziz *et al*. 2003; Bellamy *et al*. 2003; Eleni *et al*. 2009 and 2011; Willett and Beatty 2015).

For all non-pigmented and pigmented specimens, darkness storage resulted in lower hardness values than accelerated and outdoor weathering and suggests that further cross-linking as a result of UV-light exposure caused a higher polymer density and tighter polymer network which in turn made the material harder (Aziz *et al*. 2003; Bellamy *et al*. 2003; Eleni *et al*. 2009 and 2011; Willett and Beatty 2015).

4.7.2.1. Accelerated ageing

Limited literature was found on the effect of accelerated ageing on the physical and mechanical properties of maxillofacial silicones. Polyzois and Andreopoulos (1993) investigated the physical and mechanical properties of Cosmesil SM4 and HC2 (Cosmedica Ltd., Cardiff, UK) before and following accelerated ageing for 200 hours in a weathering chamber and stated that tensile strength and percent elongation increased when comparing non-weathered (control) with weathered samples. However, tear strength and hardness decreased for Cosmesil SM4 but increased for Cosmesil HC2. Despite different materials and methodology used, these observations were similar to those of the current study apart from percent elongation which decreased for all M511 specimens.

Dootz *et al.* (1994) also investigated the mechanical properties of Cosmesil following 900 hours of accelerated ageing in a weathering chamber and obtained decreased tensile strength and percent elongation as well as increased tear strength and hardness. These observations are different to those reported by Polyzois and Andreopoulos (1993). However, this may be related to three different types of Cosmesil being tested in these studies. It may be that the effects of UV-light on the internal polymer structure varied and in turn resulted in different effects on the mechanical properties of the elastomer.

Tram Nguyen *et al*. (2013) and Dootz *et al.* (1994) both conducted research on the mechanical properties of non-pigmented and pigmented MDX-4-4210 (Dow Corning) for 900 hours and total irradiance of 450 kJ m^{-2}, respectively. Tram Nguyen *et al*. (2013) reported a decrease of all recorded mechanical properties for non-pigmented specimens whereas Dootz *et al.* (1994) stated an increase of tear strength and hardness. These observed differences may be the result of different methodology.

Tram Nguyen *et al*. (2013) also used a UV mineral-based light-protecting agent (LP; Colore Science) as opacifier when investigating the physical properties of coloured MDX-4-4210 following accelerated ageing and observed significant decrease in tensile strength, tear strength, percent elongation and hardness. Application of this opacifier should be treated with caution as the measured values for all mechanical properties drastically dropped by as much as 50% which could adversely affect the performance of a facial prosthesis in clinical service.

4.7.2.2. Outdoor weathering and storage in darkness

More literature was identified on the effects of outdoor weathering and darkness on the mechanical properties of maxillofacial elastomer. Haug *et al.* (1992 and 1999) and Willett and Beatty (2015) investigated the effects of the above environments on the mechanical properties of non-pigmented A-2186 (Factor II).

Haug *et al.* (1992) reported increased tensile strength, hardness and decreased percent elongation and tear strength for non-pigmented A-2186. In the later study (1999), the authors reported decreased mechanical properties apart from hardness which increased following outdoor weathering. It is impossible to compare both studies directly as no summary of data was provided for mechanical properties testing in the later study.

However, the observed differences of mechanical properties may be related to use of different moulds when processing the elastomer. In the study from 1992, aluminium moulds were utilised but dental stone moulds used in the later study

from 1999. A-2186 is a platinum catalyst curing elastomer and these are known to be affected by impurities which in turn may have resulted in altered mechanical properties. In this current study PTFE lined moulds have been used in order to prevent any influence of impurities related to the mould type on the mechanical properties of M511 silicone.

Haug *et al.* (1999) also investigated the effects of colourants, outdoor weathering and darkness on the mechanical properties of A-2186 and reported that both had varying effects. Statistically significant increase of tensile strength and percent elongation was observed for outdoor weathered samples coloured with rayon flocking; a decrease was measured in comparison with the control group when using liquid cosmetic.

The effect of colouring and environment on the tear strength of A-2186 was inconclusive but hardness increased significantly over time and again with weathering. The authors showed that both outdoor weathering and darkness storage affected the mechanical properties of A-2186 and concluded that these effects were inherent in the elastomer and not influenced by environments. The authors suggested that changes were caused by impurities incorporated during the manufacturing process, by chemical reaction products, initiators or some other mechanism. Similar observations were made in this current study were both outdoor weathering and darkness storage altered the mechanical properties of M511 non-pigmented and pigmented elastomer.

Willett and Beatty (2015) investigated in a recent study the effects of outdoor weathering and darkness storage for 3000 hours on the mechanical properties of non-pigmented A-2186 and reported increase of tensile strength for both tested environments and slightly increased hardness following outdoor weathering. They further observed decreased modulus of elasticity for both environments and a decrease of percent elongation for samples stored in darkness, and an increase of this property following outdoor weathering. The authors based their observed changes on the combined effects of cross-linking and chain scission within the

polymer network as also suggested by Eleni *et al.* (2011) and Hatamleh *et al*. (2011).

Eleni *et al.* (2009 and 2011) and Al-Harbi *et al.* (2015) conducted research on the effect of outdoor weathering on TechSil S25 (Technovent). Eleni *et al.* (2009 and 2011) performed weathering in two locations, Thessaloniki and Athens (Greece), for a period of one year whereas Al-Harbi *et al.* (2015) conducted their investigations in Dammam (Saudi Arabia) for six months. Eleni *et al*. (2009 and 2011) concluded that modulus of elasticity and hardness both increased with outdoor weathering whereas tensile strength decreased and related their observations to increased cross-linking as a result of irradiation.

Al-Harbi *et al*. (2015) obtained similar observations with a decrease of tear strength, tensile strength, modulus of elasticity and percent elongation following outdoor exposure of TechSil S25 in a hot and humid climate. The authors also explained and related their results to alterations in the chemical structure of polymer chains as previously stated by Eleni *et al.* (2009 and 2011) and Hatamleh *et al.* (2011). However, despite the different weathering locations and weathering conditions in the above studies as well as the current study, changes in mechanical properties of maxillofacial elastomers as a result of exposure to different environments have been evident.

4.7.3. Effect of different extra-oral environments

In this current study, it was shown that accelerated ageing, natural outdoor weathering and storage in darkness affected the physical and mechanical properties of M511 elastomer at varying degrees. However, a facial prosthesis in clinical service involves a combination of numerous environments which includes beside exposure to natural and artificial day light the exposure to skin secretions as a facial prosthesis is in direct contact with natural skin. It further involves factors such as air pollution as well as those environments that are directly related to patients' habits such as smoking and prosthesis cleaning procedures

(Abdelnnabi *et al.* 1984; Hatamleh *et al.* 2011; Haug *et al.* 1999; Polyzois *et al.* 2000; Tram Nguyen *et al*. 2013; Willett and Beatty 2015).

Polyzois *et al.* (2000) investigated the effect of simulated skin secretions on the mechanical properties of Episil (Dreve-Dentamid). Test specimens were stored in simulated alkaline and acidic perspiration as well as sebum for a period of six months and statistically significant changes of tensile strength and hardness were observed. These mechanical properties changes were associated with possible increased cross-linking during the ageing period and the resultant higher density within the polymer network and are in agreement with other studies (Al-Harbi *et al.* 2015; Eleni *et al.* 2009 and 2011). However, no significant changes were measured for tear strength.

Hatamleh *et al.* (2011) conducted research on the effect of a variety of extra-oral environments on the mechanical properties of TechSil S25 (Technovent) and stated that tensile strength, tear strength, percent elongation and hardness statistically significantly changed when comparing weathered with non-weathered (control) samples. The authors further stated that these changes in mechanical properties varied which was dependant on the environment type. However, tensile strength and hardness were most affected by mixed environments including accelerated ageing and sebum.

Research has been undertaken on the effects of separate extra-oral environments (Dootz *et al.* 1994; Haug *et al*. 1992; Hatamleh *et al*. 2011; Polyzois and Andreopoulos 1993; Tram Nguyen *et al*. 2013); however, currently there is no research available on their combined effect. Furthermore, the reviewed literature only involved in-vitro testing but facial prostheses in clinical service are in contact with natural skin when the patient wears the prosthesis on a daily basis. They are also carefully peeled away from the skin daily for cleaning procedures and stored overnight whilst the patient is asleep. It is impossible to simulate these settings in any in-vitro study and only the use of an in-vivo study would provide realistic values and estimates on the effects of extra-oral environments on the mechanical properties of elastomers and consequently on the life expectancy of

facial prostheses in clinical service. This research approach would be most effective but at the same time most challenging to conduct.

Lai and Hodges (1999) investigated the effects of processing parameters on the mechanical properties of A-2186, non-pigmented and pigmented with buff pigment, kaolin and rayon flocking (Factor II). The authors processed the elastomer in stainless steel as well as in dental stone moulds and applied two different silicone polymerisation cycles. Lai and Hodges stated that all different environments had varying effects on the mechanical properties of A-2186; one of the most significant results was that except for tear strength, the mechanical properties of A-2186 cured in stainless steel moulds were significantly higher than those cured in dental stone.

Similar observations were obtained for pigments, with non-pigmented samples demonstrating better mechanical properties when compared with pigmented samples. It was further shown that curing conditions only had a significant effect on the hardness. This shows that processing also has an influence on the mechanical properties and needs to be considered when evaluating the physical and mechanical properties of maxillofacial elastomers.

Kheur *et al*. (2012) is the only paper identified looking at hardness of M511 elastomer, the same elastomer that was used in this current study, and another maxillofacial silicone elastomer (Z004) coloured with Cosmesil pigments (Technovent). The authors cured elastomer at both, room and elevated temperature, and specimens were subsequently exposed to natural outdoor weathering in Pune, India, and stored in darkness for a period of nine months. Kheur *et al*. showed with regards to the curing temperature that room temperature cured specimens demonstrated smaller changes in hardness than the heat cured specimens for both tested elastomers.

When comparing both elastomers, M511 underwent greater hardness changes within the first three months of the testing period; however, after nine months both elastomers demonstrated progressive hardening with higher hardness values

obtained for Z004. These results are in agreement with the observations made on the hardness changes of M511 in this current study. Though outdoor testing involved two very different climates (India and UK), increased hardness was measured in both studies and may be related to increased cross-linking and polymer density as a result of irradiation and time.

4.8. Conclusion

It can be concluded that both, storage in darkness and exposure to UV-light, as well as the use of pigments in the colouring process of silicone all affect the physical and mechanical properties of maxillofacial elastomer. Furthermore, it was shown that accelerated ageing in a weathering chamber resulted in largest effects on the physical and mechanical properties of elastomer. The observations made in this part of the research will add valuable information on currently available maxillofacial elastomers and may aid clinicians when choosing elastomer and colourants in the manufacturing process of facial appliances.

INSTRUMENTAL AND VISUAL ASSESSMENT OF COLOUR MATCH BETWEEN SKIN COLOURED SILICONE AND NATURAL SKIN

5.1. Introduction and aims of investigations

The degree of colour match between facial prostheses and the surrounding natural skin dictates the overall acceptance of such appliances by patients and is a direct indication for successful maxillofacial prosthetic treatment (Thomas 2006; Troppmann *et al*. 1996). However, mimicking the appearance of natural skin in silicone elastomer is a great challenge to the clinician and depends upon various variables including the skills and expertise of the person undertaking the colour matching, the inconsistency of appearance of skin, and the lighting conditions or environments under which a colour match is performed or the final prosthesis is worn (Coward *et al.* 2008; Seelaus *et al*. 2011; Troppmann *et al.* 1996; Wolfaardt 2003).

Currently, the most common practice of colour matching involves the arbitrary method of trial and error, where based on the expertise of the clinician pigments are chosen and added at varying amounts to the elastomer in several stages until a good colour match is achieved. However, this approach is time consuming and the colour match result is also unpredictable and not easily repeatable. Attempts have been made to quantify this process by using colour charts and prefabricated skin colour shade guides (Aina *et al.* 1978; Duncan and Rommerdale 1980; Guttal 2009; Over *et al*. 1998; Thomas 2006).

Whereas the above methods could help to improve the colour matching process and its results; the effect of metamerism, however, could not be controlled and requires a more scientific approach. It has been shown that skin colour can be measured utilising spectrophotometry and using this spectral data in colour formulation routines can assist to predict the colourants that would be required to colour match maxillofacial silicone elastomer with natural skin (Coward *et al.* 2008; Seelaus *et al*. 2011; Troppmann *et al*. 1996; Wolfaardt *et al*. 2003).

The aim of this part of the study was to investigate whether the use of colour formulation software would result in better colour matching results when compared with the traditional method of trial and error.

5.2. Materials and methods

5.2.1. Materials

The materials utilised in this part of the study are summarised in Table 5.1.

Material	Manufacturer
M511, Addition (Platinum) Silicone Rubber	Technovent Ltd., Bridgend, South Wales, UK
Spectromatch Pro colouring system comprised of: Titanium White, Alizarin Crimson, Logwood Maroon, Indian Yellow, MeSi Green, Malachite Green, Dinglers Green, Goethe Brown, Rubens Brown, Sinoper Brown, Tyrian Purple, Academy Blue, Apples Black	Spectromatch Ltd., Bath, UK

Table 5.1: Materials used in this part of the study.

5.2.2. Design of the study

This part of the study involved participation of subjects; ethical approval was obtained through King's College Hospital (R&D number: KCH11-127) and the Integrated Research Application System (IRAS) as 11/LO/1013 (Appendix F). All required forms including a flow chart of research methodology (Appendix G), information sheet for participants (Appendix H) as well as the consent form (Appendix I) are provided on the CD which is enclosed with this thesis. Following ethical approval, an official email was sent from the King's College London (KCL) research department to all staff and students; furthermore, posters were positioned at different locations at the Guy's Campus, KCL. Interested

subjects were invited for an initial meeting, where detailed information on the aims and objectives of the project as well as on the involved procedures was provided. Informed consent was sought from all participants before initiating any procedures involved in this colour assessment research project.

This part of the study was performed to investigate whether colour formulation software produces improved colour matches when compared with the traditional method of trial and error. It involved recording of spectral reflectance data of natural skin from 30 subjects of each of three different ethnic groups (Caucasian, C; Asian, A; and Afro/Afro Caribbean, AfC) by using a spectrophotometer (CM-2600d; Konica Minolta Sensing, Japan) and colorimeter (Colour Reader CECF-9; Konica Minolta). All recorded data was converted into L*a*b* values for use with the colour formulation software. At the time of skin colour measurement, which has been defined as time 1 (t_1), traditional colour matching was performed for all subjects (n=90).

Based on the recorded L*a*b* values, individual skin colour recipes were subsequently generated for all 90 subjects utilising Spectromatch Pro, and skin coloured silicone specimens fabricated (n = 90 based on spectrophotometer readings; n = 90 based on colorimeter readings). The colour of all fabricated silicone specimens was measured using the spectrophotometer. Furthermore, the degree of colour match between skin coloured silicone samples and natural skin was assessed using visual colour assessment with five judges of which two were lay persons and three were clinicians experienced in maxillofacial prosthetics. A total of 270 specimens (30 specimens per ethnic group and per colour matching method) were assessed for their colour and colour match with the surrounding natural skin.

At the time of visual colour assessment, which has been defined as time 2 (t_2), the skin colour of all subjects was measured again with the spectrophotometer and colorimeter in order to determine whether time has an effect on the repeatability of skin colour measurements and the colour matching result. Fig. 5.1 represents a flow chart to demonstrate the sequence of experiments.

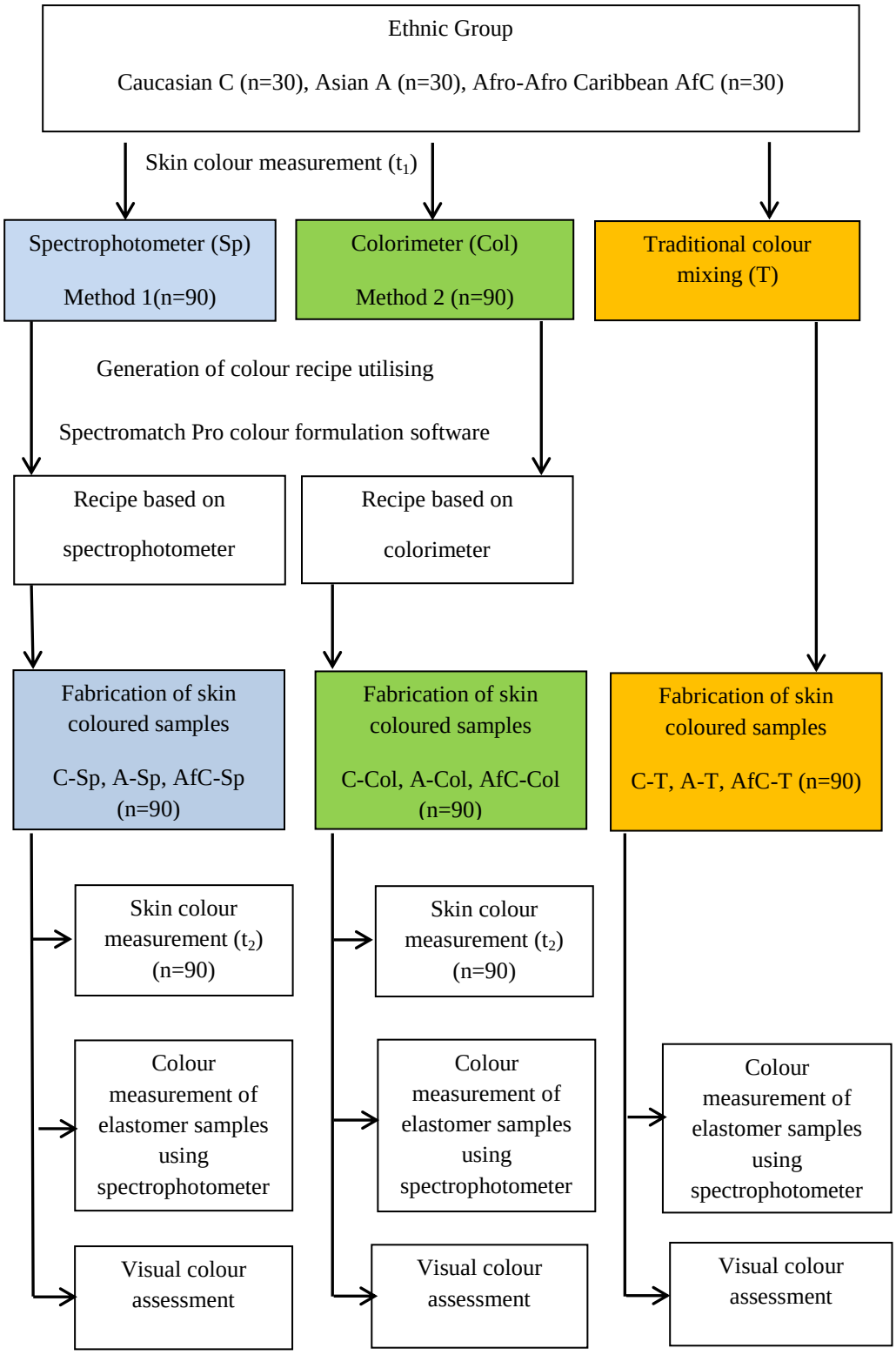


Fig. 5.1: Design of study.

5.2.3. Instrumental skin colour measurement

For each participant, skin colour was recorded using a spectrophotometer and colorimeter. Both instruments were sent to Konica Minolta for calibration prior to commencement of this study; in addition, both instruments were calibrated at any time of skin colour measurements in accordance to the manufacturer instructions, using a white and black calibration background.

Each subject was seated in the room where the spectral data was recorded for at least 15 min to acclimatise to the room temperature which was maintained at 21°C ± 2°C. An area of the supine forearm was chosen for recording the spectral reflectance curves as it provides a flat and easily accessible area of skin and is also considered to be representative of a subjects' base skin colour. Furthermore, this area faces away from direct sunlight and is therefore at a lower risk to undergo skin colour changes due to tanning. Areas of skin with blemishes, freckles, varying colouration and excessive vasculature were avoided.

A cross mark was drawn on the subjects' left forearm using an indelible pencil, 5 cm away from the arm bend and 2 cm away from the major blood vessels and is shown in Fig. 5.2. Four spectral measurements per instrument were recorded of the selected skin area, one measurement on each side of the marking (Figs. 5.3 and 5.4). The recorded data was transferred to the Colour Calculation software (Spectromatch); measurements were only accepted when all four recordings were within a colour difference tolerance of 0.5 ΔE and subsequently averaged to produce one L*a*b* recording per instrument and subject which was then used to generate individual skin colour recipes utilising the Spectromatch Pro colour formulation software. All colour measurement data was entered onto an Excel spreadsheet for further use and saved anonymously (applying a number coding), in a password protected file and office computer.

Fig. 5.2: Skin area and cross mark for spectral colour measurement.

Fig. 5.3: Skin colour measurement using the spectrophotometer.

Fig. 5.4: Skin colour measurement using the colorimeter.

5.2.4. Traditional method of colour mixing

The main objective of this part of the study was to compare the traditional method of colour matching with the computerised colour formulation software. For traditional colour mixing, 30 g of base polymer M511 and 3 g of cross-linker were weighed on a high precision scale with an accuracy of 0.001 g. Spatulating of the components was performed using the Speed Mixer DAC 150 FVZ-K, three times for 30 seconds at 1800 rpm to ensure homogeneity of the mix.
Thirteen colourants from the Spectromatch Pro colour palette were available for the colour mixing process. Each subject was seated on a chair opposite the clinician undertaking the mixing, with the left forearm comfortably rested. Traditional colour matching was performed under D65 daylight lighting in the laboratory, close to the window but away from direct sunlight. Based on the clinicians' expertise, various colourants at varying amounts were added to the silicone elastomer gradually and then mixed by hand until homogeneity was achieved.

The degree of colour match was checked by loading a small amount of skin coloured elastomer on a clear colour match sheet (G805, Technovent) which was then placed adjacent to the selected skin area. The procedures of pigment adding, mixing and colour match control were repeated several times until a good colour matching result was achieved. However, the clinician was given a maximum of thirty minutes for mixing the subjects' base skin colour. Colour matching sessions were scheduled between 9.00 a.m. and 2.00 p.m. to minimise physical tiredness of the subject and the clinician undertaking the colour mixing.

Once the colour matching process was completed, the elastomer was packed and polymerised as described in Chapter 3, section 3.2.1.

5.2.5. Fabrication of test specimens utilising Spectromatch Pro

Spectromatch Pro was utilised to establish individual skin colour recipes for all subjects based on the spectral reflectance readings measured with both, spectrophotometer and colorimeter. For this process, the recorded spectral data was entered into the colour formulation software and an individual colour recipe was generated for each subject and instrument.

The amount of 30 g of base elastomer M511 and 3 g of cross-linker was predetermined to allow fabrication of three coloured test specimens in case of sample inaccuracies such as air inclusions. The amount of base elastomer and cross-linker was entered into the colour formulation programme and the list of pigments and their required weight was generated. Silicone elastomer and pigments were weighed on a high precision scale with an accuracy of 0.0001 g. The amount of each pigment, base elastomer and cross-linker had to be weighed separately in several steps, and confirmed that each of the weighed components was within the allowed weight tolerance, before the next component could be added. Once all components of the individual skin colour recipe were weighed, silicone elastomer and pigments were spatulated utilising the Speed Mixer DAC 150 FVZ-K to ensure homogeneity of the mix. The elastomer was then carefully packed into the PTFE lined mould and processed as described in Chapter 3, section 3.2.1.

5.2.6. Instrumental colour measurement and calculation of ΔE

The colour of all manufactured specimens was measured using the spectrophotometer. For colour recordings, samples were located in the specially designed sample holder; spectral values were obtained and $\overline{\Delta E}$ calculated as previously described and applied in Chapter 3, section 3.2.4. A summary of ΔE comparisons is provided in Table 5.2.

Comparisons (ΔE)		
Skin measurement t_1 Spectrophotometer		Skin measurement t_1 Colorimeter
Skin measurement t_2 Spectrophotometer		Skin measurement t_2 Colorimeter
Skin measurement t_1 Spectrophotometer		Skin measurement t_2 Spectrophotometer
Skin measurement t_1 Colorimeter		Skin measurement t_2 Colorimeter
Skin measurement t_1 Spectrophotometer		Colour measurement of silicone samples based on: a) spectrophotometer, b) colorimeter, c) traditional mixing
Skin measurement t_2 Spectrophotometer		Colour measurement of silicone samples based on: a) spectrophotometer, b) colorimeter, c) traditional mixing

Table 5.2: Summary of ΔE comparisons.

5.2.7. Visual colour match assessment

This part of the study was designed to assess the colour match of manufactured silicone elastomer samples based on Spectromatch Pro, and of samples made based on the traditional colour mixing method in comparison with natural skin. Three skin coloured silicone specimens were visually assessed per subject; one for the traditional colour matching method, the second sample based on colour formulation software and the spectral data recorded with the spectrophotometer, and the third sample based on colour formulation software and the data recorded with the colorimeter.

Visual assessment of silicone specimens was carried out by five judges of whom three were practising clinicians in maxillofacial technology and two lay persons. All three clinicians had a long clinical experience in the prosthetic treatment of patients with maxillofacial defects. The two lay judges were of a different professional background and never involved with maxillofacial prosthetic rehabilitation. The judges were comprised of three men and two women.

All judges were initially assessed for colour acuity using the Ishihara Colour Blindness test (Appendix J, on CD enclosed with this thesis). Before visual colour assessment was commenced, all judges were instructed and trained on how a skin base colour is to be identified as it was previously described by Seelaus and Troppmann (2000). In addition, prefabricated skin coloured silicone samples were shown to the judges to demonstrate the colour match assessment and grading scores for a match or mismatch of silicone samples with natural skin. The judges were randomly assigned numbers and the order of their individual subject assessments was generated using a random numbers table.

Subjects were seated for at least 10 min inside the room where visual assessment was carried out in order to acclimatise to room temperature which was maintained at 21 °C ± 2°C. Colour assessment was performed utilising a standardised viewing environment in form of the Q-Lab viewing booth (Q-Lab Europe Ltd., Bolton, UK). The viewing booth was illuminated with daylight lamps (D65)

which represents the average midday daylight in Western/Northern Europe and comprises of both, direct sunlight and light diffused by a clear sky, and has a correlated colour temperature of approximately 6500 K (Hunter and Pointer). The inside of the viewing cabinet was painted with 100% coverage in a neutral grey paint (Munsell 8). For visual assessment, subjects were asked to wear a white laboratory coat in order to avoid distraction from brightly coloured clothing and were seated in front of the viewing booth, with their left supine forearm conveniently rested inside the viewing booth. A specially designed, neutral grey (Munsell 8) coloured sample holder, similar to the sample holder utilised by Seelaus *et al*. (2011) was used for colour match assessment. The sample holder had a rectangular opening that measured twice the length of a silicone sample, providing equal viewing area of the natural skin and skin coloured sample placed next to it. For colour match assessment, it was positioned on the left supine forearm of subjects and secured by gently pulling the fastening straps (Fig. 5.5).

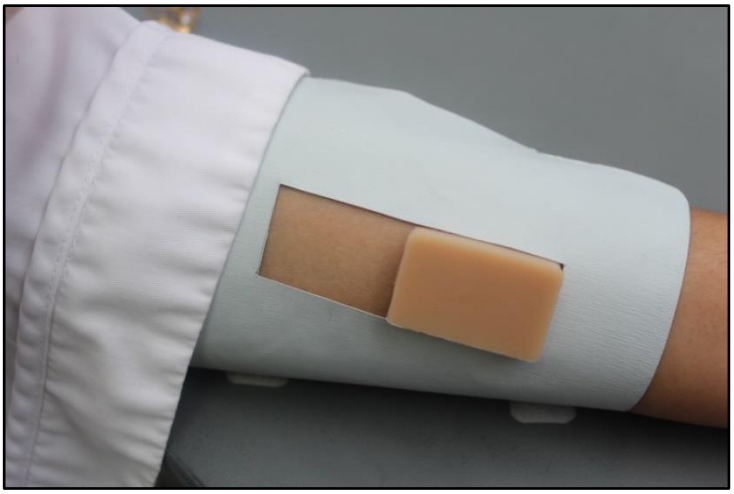


Fig. 5.5: Sample holder with positioned skin coloured sample and adjacent natural skin area.

Each of the three prepared skin coloured silicone samples was positioned on the right side within the opening of the sample holder leaving the left side exposed for colour match assessment. This exposed area of skin on the forearm represented the area where the initial spectral skin measurements were taken.

Samples were secured to the skin with G 604 edge adhesive (Technovent) to ensure their correct positioning during the colour assessment procedure. Surface gloss of silicone specimens was minimised as an attribute of appearance in the original fabrication of samples and a matt silicone surface was produced using the PTFE lined mould (Coward *et al*. 2008).

Subjects were asked to rest their left forearm with the skin coloured sample positioned at a 45° angle on the floor of the of the viewing booth; each colour assessor was 12 inches away from the viewing booth and at a height such that the observation angle was 45° from the normal to the skin coloured specimens which was in accordance to recommended standardised conditions for visual colour assessment (Berns 2000; Hunter 1987) and has been used in previous investigations (Bellini 2014; Coward *et al.* 2008).

For visual colour match assessments, judges were called individually and asked to provide a score on the degree of colour match. Possible scores included: 1 = 'very good', 2 = 'good', 3 = 'satisfactory', 4 = 'non-satisfactory' and 5 = a 'poor' colour match. Judges were given a maximum of 2 minutes to give a score for each colour match assessment.

5.2.8. Statistical analysis

The effect of instrument and ethnic group on ΔE was analysed using LMM as previously described, Chapter 3, section3.2.4.

Initial analysis of the observer 5 point scores showed that the results for 'very good' and 'poor' were sparse, and this can cause computational problems. Consequently, the scores were condensed to a 3 point scale by combining 'very good' and 'good' as 'good', and 'non-satisfactory' and 'poor' as 'poor'. The results were analysed using ordered logistic regression, allowing for repeated measurements on each subject, followed by multiple comparison test (Williams 2015).

5.3. Results

All data of skin and silicone elastomer colour measurements as well as the results of visual colour match assessment are provided in Appendix K on the CD which is enclosed with this thesis.

5.3.1. Comparison of L*a*b* values between instruments

L*a*b* values were recorded with the spectrophotometer and colorimeter for each ethnic group at t_1 and t_2. Measurements with the spectrophotometer for all ethnic groups at both times obtained L* values ranging from 37.14 to 72.63, a* values from 2.74 to 11.62 and b* values from 8.83 to 21.98. For the colorimeter, the L* values ranged from 36.84 to 73.19, a* values from 2.73 to 11.56 and b* values from 8.27 to 21.77.

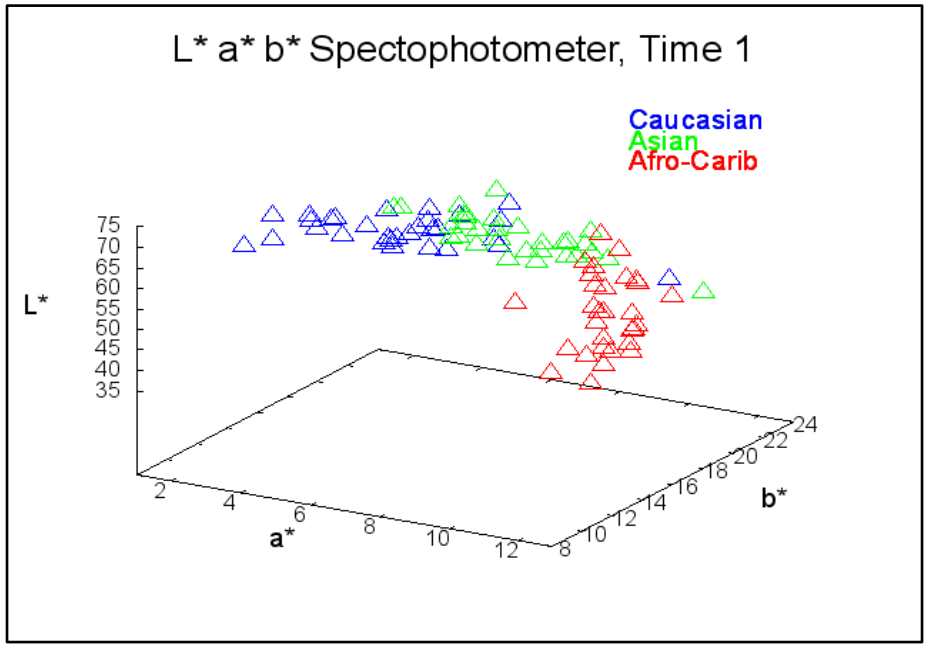
A summary of L*a*b* values for both instruments and all ethnic groups at t_1 and t_2 is provided in Tables 5.3 and 5.4. The data scatter of L*a*b* for both instrument recordings at t_1 and t_2 is shown in the corresponding figures (Figs. 5.6 (a), (b) and 5.7 (a), (b)).

			Mean, sd	min	max
C	t_1	L*	68.16, 3.83	52.45	72.25
	t_2	L*	67.90, 3.63	55.31	72.63
A	t_1	L*	62.28, 4.33	49.78	69.56
	t_2	L*	62.69, 4.20	52.87	68.78
AfC	t_1	L*	46.63, 5.26	37.14	57.89
	t_2	L*	47.42, 5.64	37.93	62.52
C	t_1	a*	5.71, 1.57	2.99	10.81
	t_2	a*	6.04, 1.59	2.74	10.30
A	t_1	a*	7.44, 1.49	4.75	11.62
	t_2	a*	7.22, 1.41	5.03	10.66
AfC	t_1	a*	9.91, 0.88	7.77	11.13
	t_2	a*	9.64, 0.87	6.56	10.96
C	t_1	b*	14.64, 2.52	9.05	20.81
	t_2	b*	14.52, 2.32	8.83	20.06
A	t_1	b*	18.37, 1.46	15.79	21.19
	t_2	b*	17.80, 1.39	15.20	19.97
AfC	t_1	b*	18.69, 1.84	15.21	21.98
	t_2	b*	18.53, 1.96	14.39	21.91

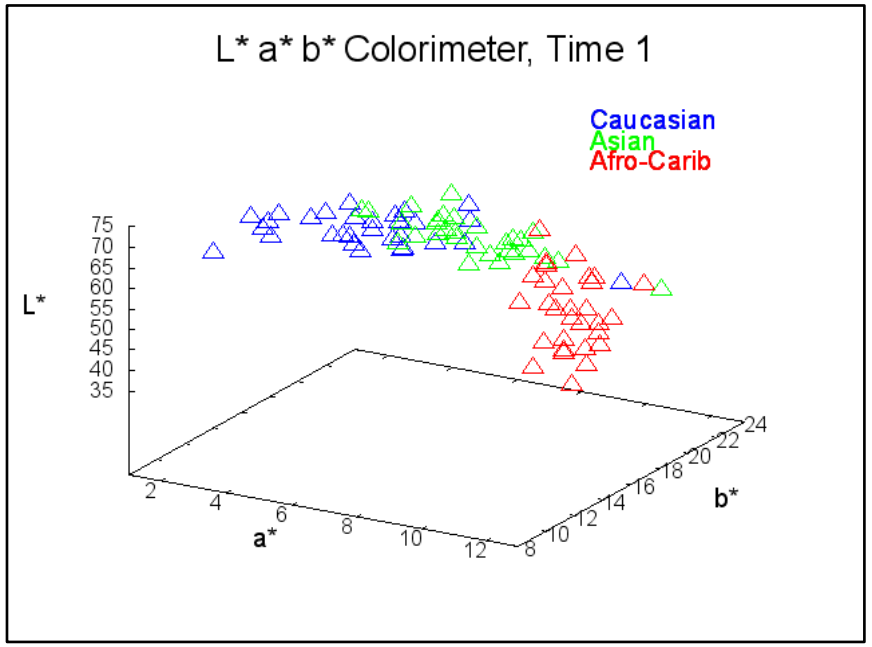
Table 5.3: Univariate summary statistics of Spectrophotometer L*a*b* for all ethnic groups at time 1 (t_1) and time 2 (t_2).

			Mean, sd	min	max
C	t_1	L*	68.48, 4.03	52.11	72.68
	t_2	L*	68.24, 3.43	56.18	73.19
A	t_1	L*	62.36, 4.30	49.88	69.85
	t_2	L*	62.89, 4.17	53.33	69.01
AfC	t_1	L*	47.00, 5.20	36.84	58.61
	t_2	L*	47.54, 5.69	37.96	62.62
C	t_1	a*	5.57, 1.57	3.01	10.72
	t_2	a*	5.76, 1.58	2.73	10.23
A	t_1	a*	7.21, 1.47	4.51	11.56
	t_2	a*	6.87, 1.45	4.27	10.01
AfC	t_1	a*	9.90, 0.97	7.79	11.28
	t_2	a*	9.57, 1.06	6.08	11.07
C	t_1	b*	14.40, 2.49	8.27	20.48
	t_2	b*	14.40, 2.30	8.82	20.24
A	t_1	b*	18.09, 1.47	15.04	21.39
	t_2	b*	17.48, 1.51	14.64	19.75
AfC	t_1	b*	18.83, 1.68	15.66	21.54
	t_2	b*	18.59, 1.80	14.88	21.77

Table 5.4: Univariate summary statistics of colorimeter L*a*b* for all ethnic groups at time 1 (t_1) and time 2 (t_2).

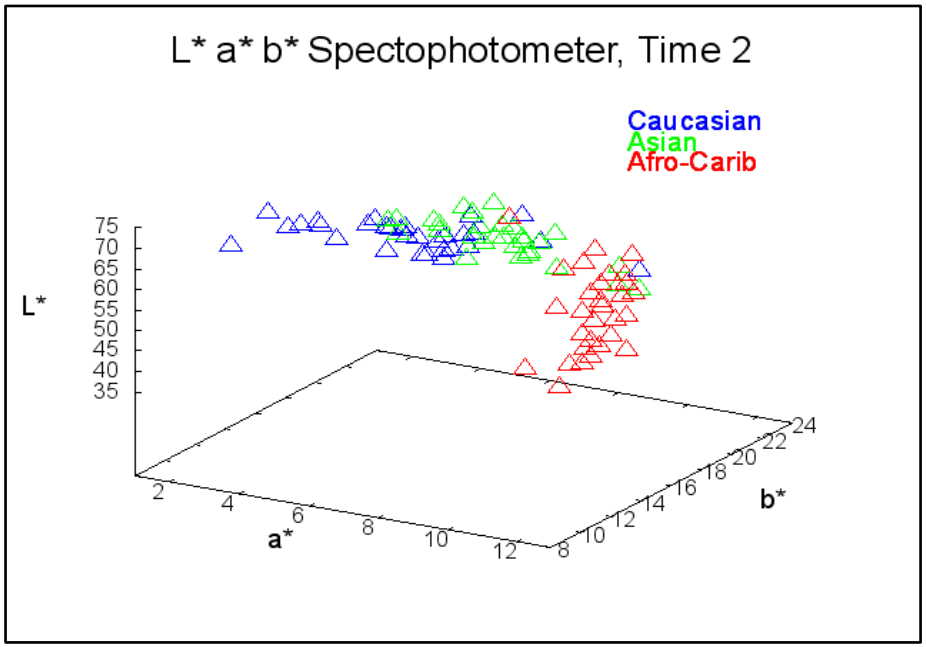


(a)

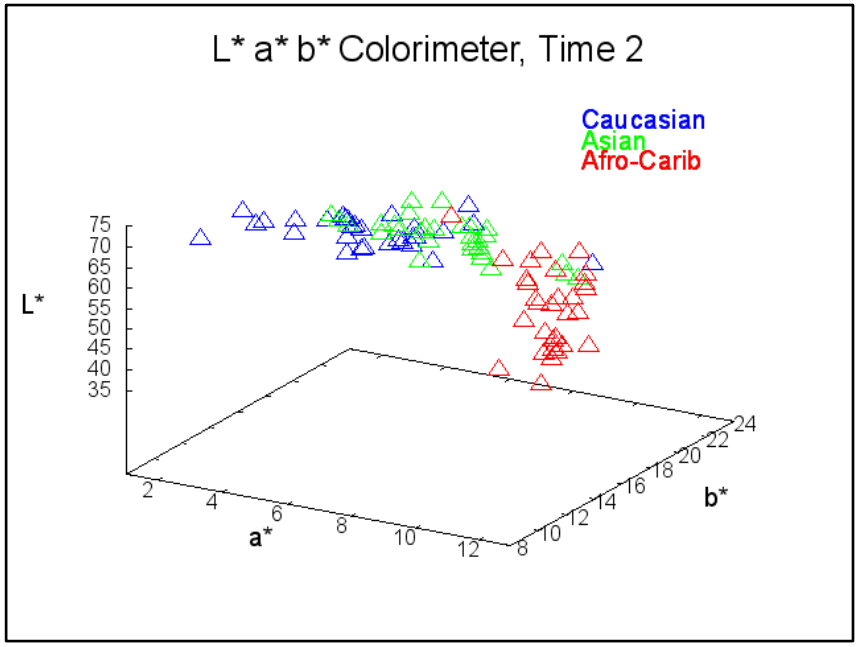


(b)

Fig. 5.6: Data scatter of L*a*b* at t_1; (a) spectrophotometer, (b) colorimeter.



(a)



(b)

Fig. 5.7: Data scatter of L*a*b* at t_2; (a) spectrophotometer, (b) colorimeter.

A paired t-test was applied to compare the L*a*b* values recorded with the spectrophotometer and colorimeter at t_1 and at t_2. Overall, there was a statistically significant effect on ΔL*, Δa* and Δb* for all ethnic groups at t_1 and t_2. A summary statistics for L*a*b*, ethnic group, and time is provided in Table 5.5.

	t_1				t_2			
		Ethnic group				Ethnic group		
	Overall	C	A	AfC	Overall	C	A	AfC
p (Sp-Col) L*	0.001	0.001	0.319	0.001	0.002	0.078	0.001	0.145
p (Sp-Col) a*	0.001	0.045	0.001	0.976	0.001	0.003	0.001	0.221
p (Sp-Col) b*	0.005	0.006	0.001	0.052	0.010	0.256	0.001	0.277

Table 5.5: Probabilities (p) for pairwise instrument comparison (Sp-Col) of colour components at t_1 and t_2, overall and for each ethnic group.

A paired t-test was applied to compare the L*a*b*values measured with the spectrophotometer at t_1 and t_2, and the colorimeter at t_1 and t_2 for each ethnic group. Overall, there was no statistically significant effect on L* and a* for both spectral instruments at t_1 and t_2. However, there was a statistically significant effect on b* for both instruments at t_1 and t_2. A summary statistics of colour components, ethnic group and instrument is provided in Table 5.6.

	Spectrophotometer				Colorimeter			
		Ethnic group				Ethnic group		
	Overall	C	A	AfC	Overall	C	A	AfC
p (t_1-t_2) L*	0.12660	0.5262	0.2166	0.0242	0.1415	0.5090	0.0841	0.0877
p (t_1-t_2) a*	0.6146	0.1217	0.1798	0.0237	0.0930	0.3435	0.0435	0.0074
p (t_1-t_2) b*	0.0170	0.6766	0.0005	0.2166	0.0147	0.9978	0.0004	0.0633

Table 5.6: Probabilities (p) for pairwise time interval comparison (t_1-t_2) of colour components (L*a*b*) for both spectral instruments, overall and for each ethnic group.

5.3.2. Comparison of $\overline{\Delta E}$ between instruments

Spectral skin measurements were obtained using the spectrophotometer (Sp) and colorimeter (Col) at t_1 and t_2. A paired t-test was applied to compare the $\overline{\Delta E}$ values for the spectrophotometer readings and the colorimeter readings, both measured at t_1 and t_2. The results showed that there was no statistically significant difference of $\overline{\Delta E}$ between spectrophotometer and colorimeter measurements (Sp - Col) at both times. Furthermore, there was no statistically significant difference between $\overline{\Delta E}$ of spectrophotometer readings, and of colorimeter readings at both times. The $\overline{\Delta E}$ for both instruments, standard deviation (sd) and probability (p) are summarised in Table 5.7. The distribution of ΔE as ordered deviations from the $\overline{\Delta E}$ between instruments and for both instruments at t_1 and t_2 are shown in Figs. 5.8 and 5.9.

Comparison	$\overline{\Delta E}$	sd	p
Sp t_1 – Col t_1	0.71	0.36	0.552
Sp t_2 – Col t_2	0.75	0.58	
Sp t_1 – Sp t_2	2.00	1.45	0.068
Col t_1 – Col t_2	1.85	1.35	

Table 5.7: Univariate summary statistics for comparison of spectral instruments (Sp, Col) at t_1 and t_2 and the associated probability, p, for their comparison.

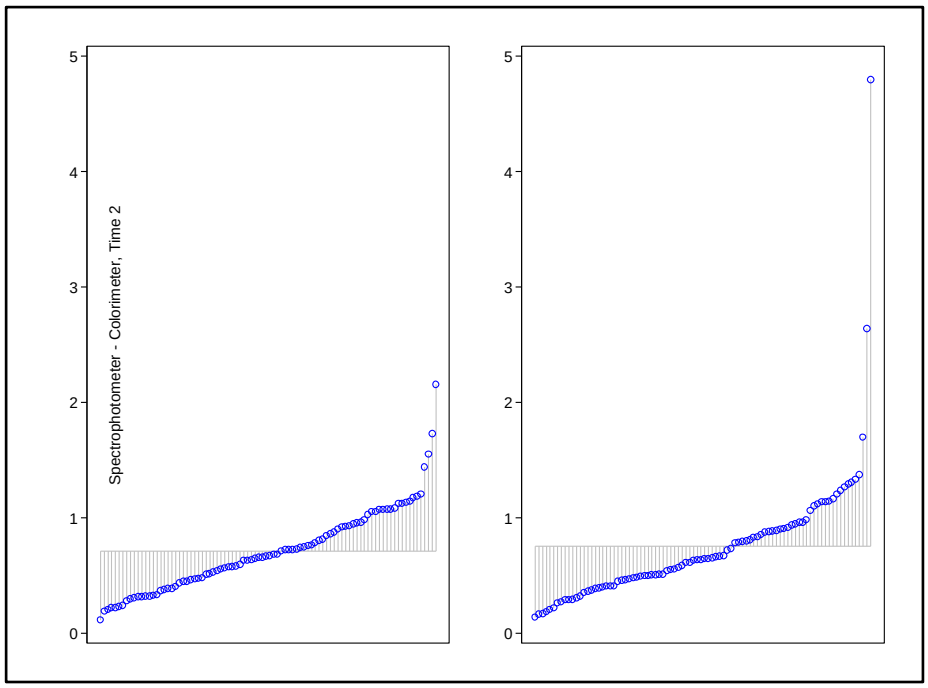


Fig. 5.8: Deviation plots for ΔE between instruments at t_1 and t_2.

The plots show the deviation of each data point from $\overline{\Delta E}$ in ascending order.

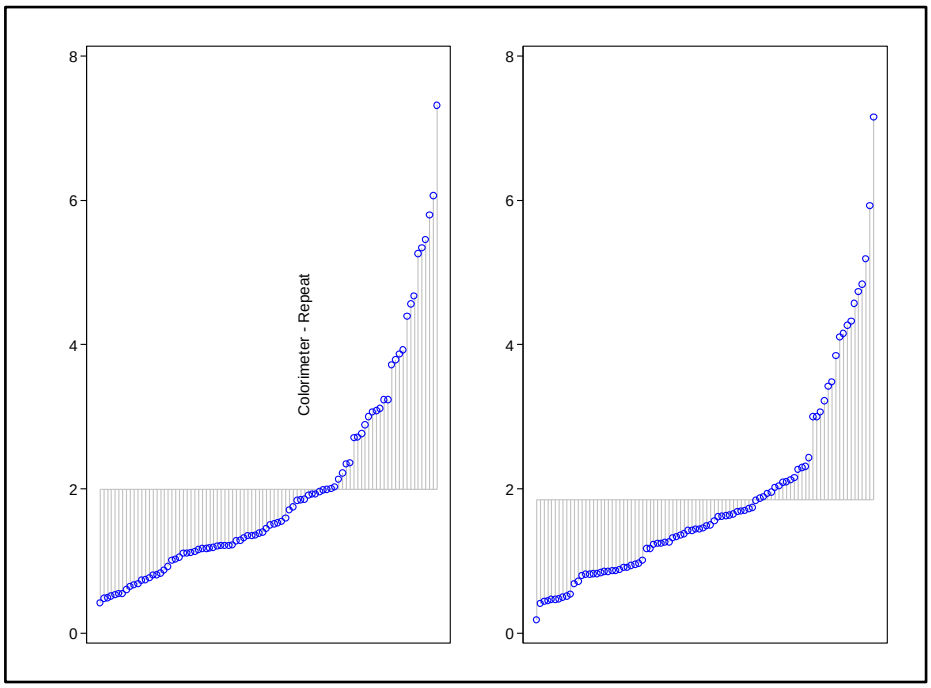


Fig. 5.9: Deviation plots for ΔE for each instrument instruments at t_1 and t_2.

The plots show the deviation of each data point from $\overline{\Delta E}$ in ascending order.

ΔE is a calculated value derived from a colour difference function which makes using it for agreement difficult if not impossible. Concordance of $\overline{\Delta E}$ between t_1 and t_2 for instruments per ethnic group is shown in Fig. 5.10; and between instruments at t_1 and t_2 per ethnic group in Fig. 5.11.

A summary of calculated minimum and maximum $\overline{\Delta E}$ values for both instruments, overall and per ethnic group is shown in Appendix L, Table 1. $\overline{\Delta E}$ in relation to elapsed time, overall and per ethnic group is shown in Appendix L, Figs. 1 to 4.

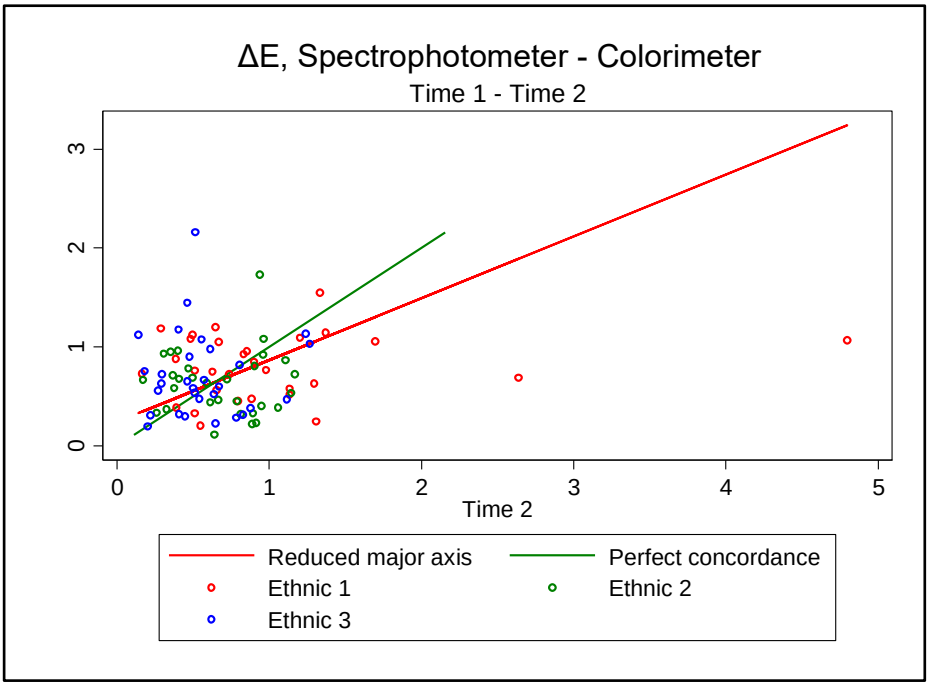


Fig. 5.10: Concordance of $\overline{\Delta \mathbf{E}}$ between t1 and t2 for instruments per ethnic group.

(Ethnic 1 = C, Ethnic 2 = A, Ethnic 3 = AfC)

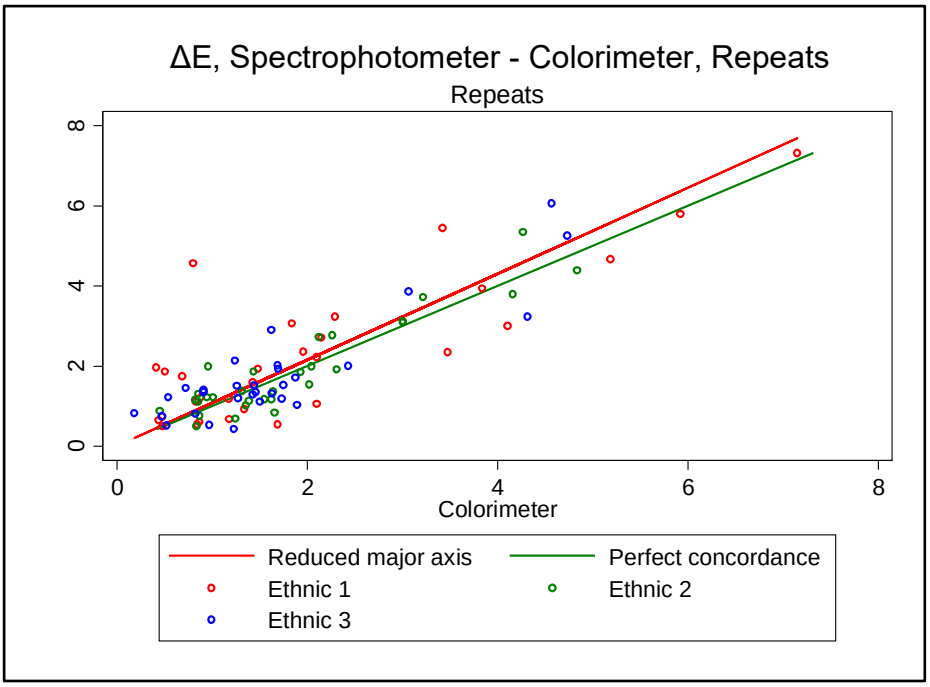


Fig. 5.11: Concordance of $\overline{\Delta \mathbf{E}}$ between instruments at t_1 and t_2 per ethnic group.

(Ethnic 1 = C, Ethnic 2 = A, Ethnic 3 = AfC)

5.3.3. Comparisons of $\overline{\Delta E}$ between skin and silicone samples

$\overline{\Delta E}$ were calculated for comparison of skin measurements recorded at time $_1(S_1)$ and at time $_2$ (S_2) with manufactured samples at t_1 $(S_1 – T, S_1 – Sp, S_1 – Col)$ and at t_2 $(S_2 – T, S_2 – Sp, S_2 – Col)$. A summary table of $\overline{\Delta E}$ for comparison of skin and silicone samples for each ethnic group at t_1 and t_2 is shown in Table 5.8.

Ethnic Groups	t_1			t_2		
	$\overline{\Delta E}$			$\overline{\Delta E}$		
	S_1 - T	S_1- Sp	S_1 - Col	S_2 - T	S_2 - Sp	S_2 - Col
C	3.46	1.46	1.64	3.57	2.74	2.81
A	4.05	1.13	1.30	4.08	2.44	2.38
AfC	4.88	0.79	1.01	4.85	1.90	1.87

Table 5.8: $\overline{\Delta E}$ between skin and manufactured skin coloured samples for each ethnic group at t_1 and t_2.

LMM analysis was applied and showed that there was a statistically significant effect of sample comparison ($p = 0.001$) and no statistically significant effect of ethnicity. However, there was a statistically significant interaction between sample comparison and ethnic group at both, t_1 and t_2 (Table 5.9).

	t_1	t_2
Skin – sample comparison	0.001	0.001
Ethnic groups	0.953	0.833
Skin – sample comparison # ethnic group	0.001	0.001

Table 5.9: Summary of LMM analysis showing main effects for comparison and ethnic groups, and the comparison#ethnic group interaction.

Šídák's multiple comparisons of means test showed that there was only a statistically significant difference between Skin at both times and samples based

on the traditional approach of colour mixing ($p = 0.001$). Furthermore, there was no statistically significant effect for t_1 and t_2 for all ethnic groups.

Predictive margins for $\overline{\mathbf{\Delta E}}$ of sample comparisons and 95% confidence intervals for all ethnic groups at t_1 and t_2 are shown in Figs. 5.12 and 5.13.

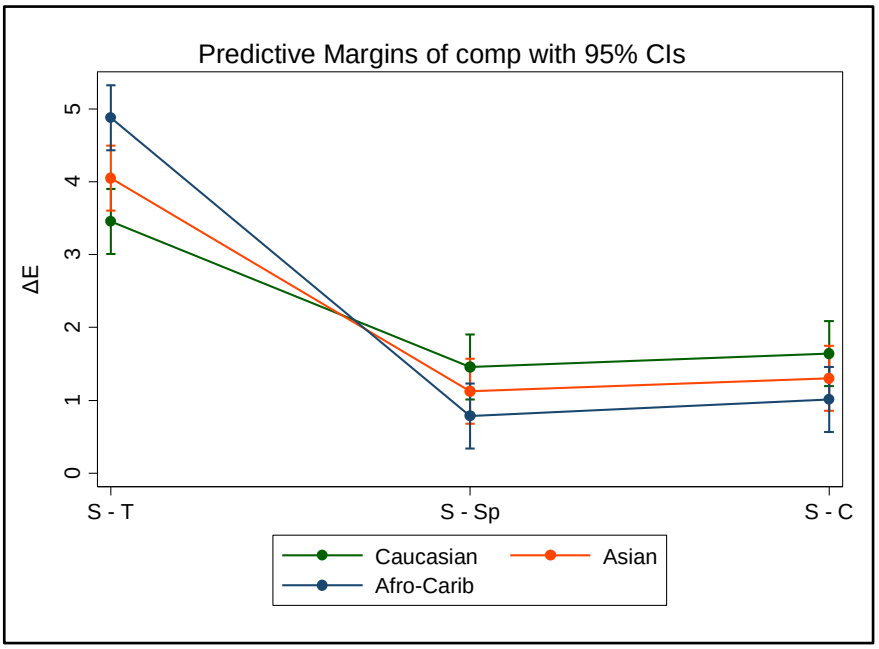


Fig. 5.12: $\overline{\mathbf{\Delta E}}$ for sample comparisons and associated 95% confidence intervals for all ethnic groups at t_1.

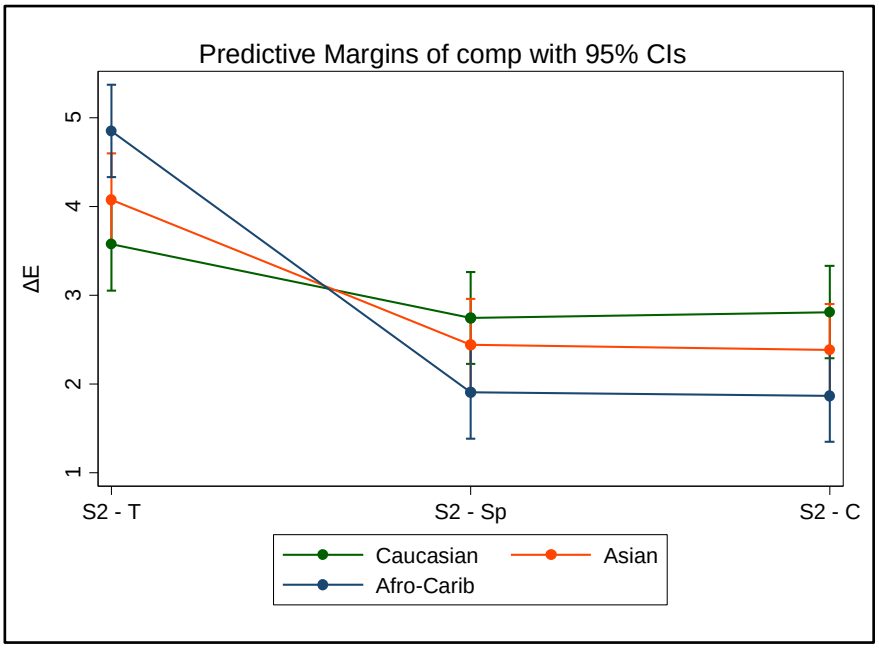


Fig. 5.13: $\overline{\mathbf{\Delta E}}$ for sample comparison and associated 95% confidence intervals for all ethnic groups at t_2.

5.3.4. Comparisons of samples involving PT and AT

Statistical analysis showed that there was a statistically significant effect of colour matching method ($p = 0.001$) on the PT and AT. However, there was no statistically significant effect of ethnic group on PT ($p = 0.202$) and AT ($p = 0.465$). $\overline{\Delta E}$ between original skin colour readings and silicone samples based on the three colour matching methods were calculated (S – T, S – Sp, S – Col). A summary on how many skin- silicone sample comparisons (n) from a total of 90 comparisons (colour matching method and ethnic groups) were below and above PT and AT is shown in Table 5.10. A summary of data for sample comparisons and ethnic groups in relation to PT and AT are illustrated in Figs. 5.14 to 5.17.

		Colour matching method			Ethnic group		
		S – T (n)	S – Sp (n)	S – Col (n)	C (n)	A (n)	AfC (n)
PT	< 1 ΔE	2	51	39	26	29	37
	> 1 ΔE	88	39	51	64	61	53
AT	< 2 ΔE	11	82	78	53	57	61
	> 2 ΔE	79	8	12	37	33	29

Table 5.10: Summary data for number of comparisons (n) below and above PT and AT for colour matching method and ethnic group.

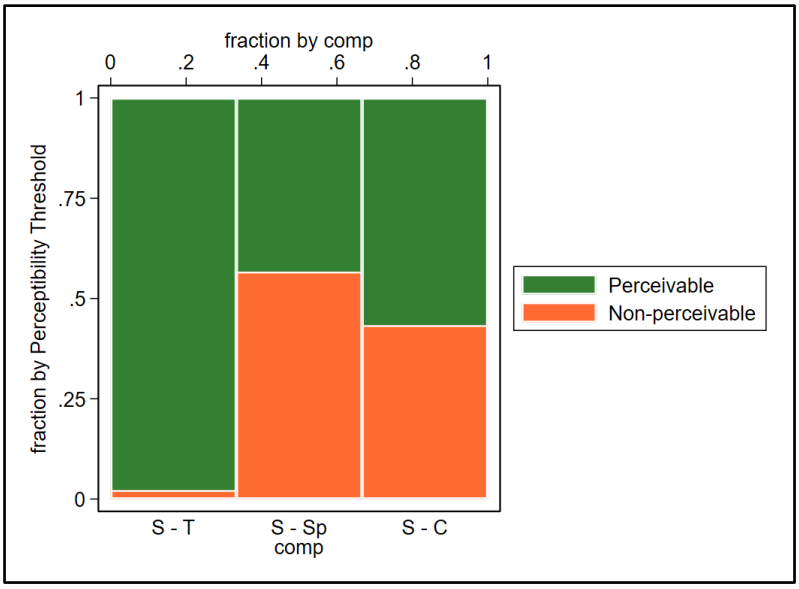


Fig. 5.14: Spine plot of non-perceivable (below PT) and perceivable (above PT) skin versus sample comparisons per method.

The area of each tile is proportional to the count for each combination of perceivability and comparison.

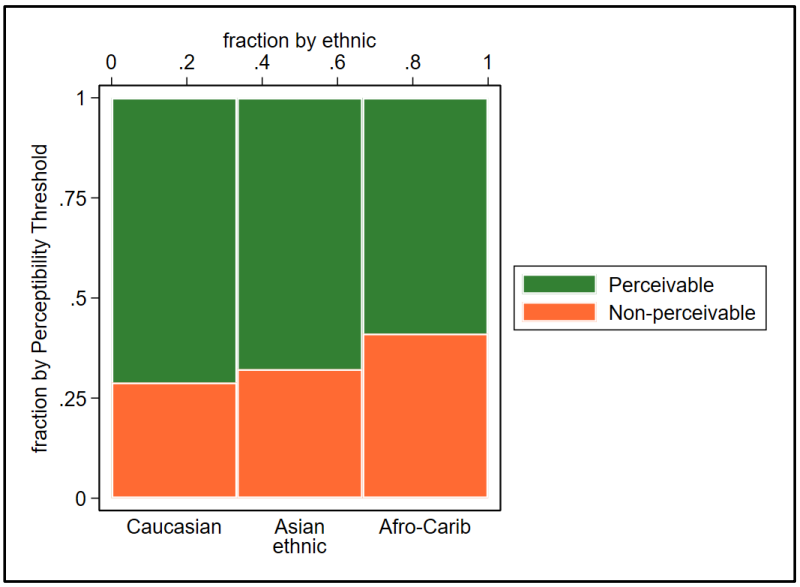


Fig. 5.15: Spine plot of non-perceivable (below PT) and perceivable (above PT) skin versus ethnic group.

The area of each tile is proportional to the count for each combination of perceivability and ethnic group.

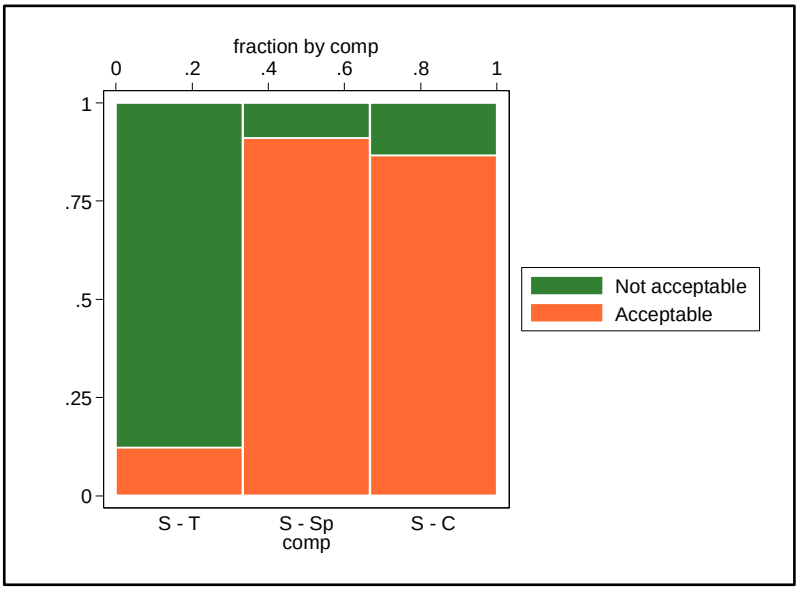


Fig. 5.16: Spine plot of acceptable (below AT) and not acceptable (above AT) skin versus sample comparisons per method.

The area of each tile is proportional to the count for each combination of acceptability and comparison.

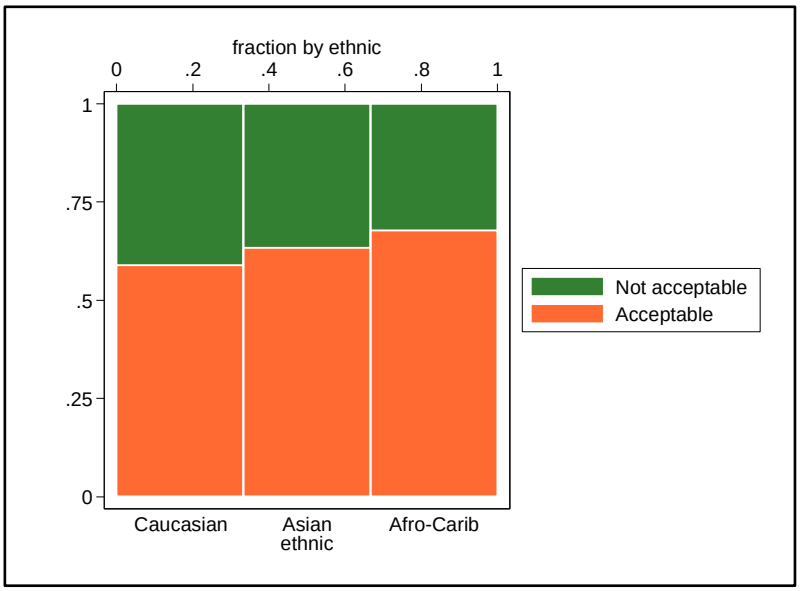


Fig. 5.17: Spine plot of acceptable (below AT) and not acceptable (above AT) skin versus sample comparisons per ethnic group.

The area of each tile is proportional to the count for each combination of acceptability and ethnic group.

5.3.5. Visual assessment of colour match

Visual assessment of colour match between skin coloured silicone specimens, which were produced based on traditional and computerised colour matching methods, and natural skin was performed using five judges. Judges provided a score from 1 to 5 on the degree of colour match for each presented silicone sample; these were condensed to 3 scores for statistical analysis.

LMM analysis was applied and showed that there was a statistically significant effect of colour matching method, judge and the interaction judge and ethnic group ($p = 0.001$). Ethnic group itself did not have a statistically significant effect as a main factor but was involved as an interaction term with judge (Table 5.11).

	probability (p)
Colour matching method	0.001
Judge	0.001
Colour matching method # judge	0.028
Ethnic group	0.140
Colour matching method # ethnic group	0.434
Judge versus ethnic group	0.001
Colour matching method # judge # ethnic group	0.661

Table 5.11: Summary of LMM analysis involving colour matching method, judge, ethnic group and their interactions.

Šídák's multiple comparisons of means test was applied when comparing the main effects (colour matching method, judges, and ethnic groups) and showed that traditional mixing was statistically significantly different from the other colour matching methods and that there was no difference between judges 2, 3 and 4; however, judges 1 and 5 were statistically significantly different from each other (Table 5.12).

		Šídák groups
Judge	1	
	2	A
	3	A
	4	A
	5	
Colour matching method	T	
	Sp	A
	Col	A
Ethnic group	C	A
	A	A
	AfC	A

Table 5.12: Šídák's multiple comparison of the main effects of Judges, colour matching method and ethnic group.

(Judges: 1 – 5; colour matching method: T – traditional, Sp – spectrophotometer, Col – colorimeter; ethnic groups: C – Caucasian, A – Asian, AfC – Afro/Afro-Caribbean)

Groups sharing the same letter are not statistically significantly different.

Šídák's multiple comparisons test was also applied to analyse interactions between judge, colour matching method, judge and ethnic group and showed there was no statistically significant difference and no obvious pattern (Table 5.13).

Judge # colour matching method	Šídák groups	Judge # ethnic group	Šídák groups
1 # T	E	1 # C	BCD
1 # Sp	ABCD	1 # A	BCD
1 # Col	ABC	1 # AfC	BCD
2 # T	BCDE	2 # C	BC
2 # Sp	A	2 # A	ABC
2 # Col	A	2 # AfC	ABC
3 # T	ABCDE	3 # C	AB
3 # Sp	AB	3 # A	ABC
3 # Col	AB	3 # AfC	BC
4 # T	ABCD	4 # C	A
4 # Sp	ABC	4 # A	BCD
4 # Col	AB	4 # AfC	BCD
5 # T	E	5 # C	CD
5 # Sp	DE	5 # A	BCD
5 # Col	CDE	5 # AfC	D

Table 5.13: Šídák's multiple comparison of the interactions between Judges, colour matching method and ethnic group.

Groups sharing the same letter are not statistically significantly different.
(Judge: 1 – 5; method: T – traditional, Sp – spectrophotometer, Col – colorimeter; ethnic groups: C – Caucasian, A – Asian, AfC – Afro/afro-Caribbean)

Summary of all data for judges versus scores is illustrated in Fig. 5.18. Furthermore, summary plots of data for judges versus scores for all ethnic groups are provided in Figs. 5.19 to 5.21.

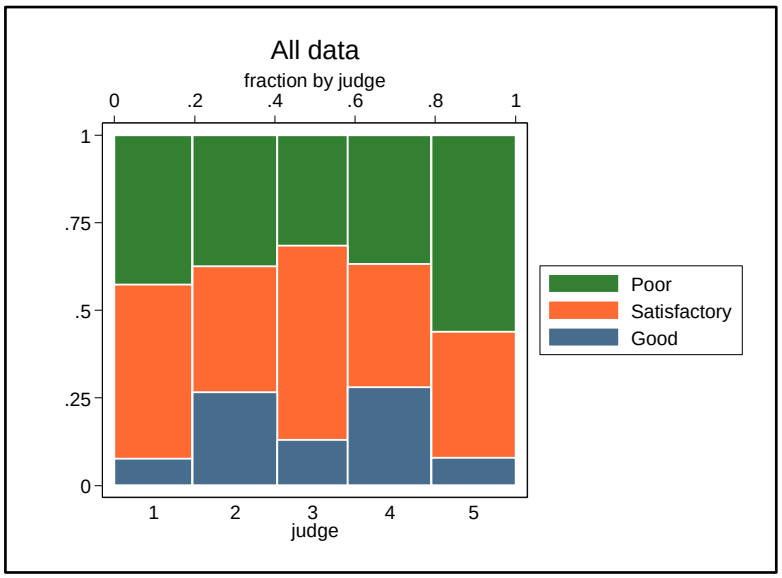


Fig. 5.18: Spine plot of judges and scores for the data combined over all ethnic groups.

The area of each tile is proportional to the count for each combination of judge and score.

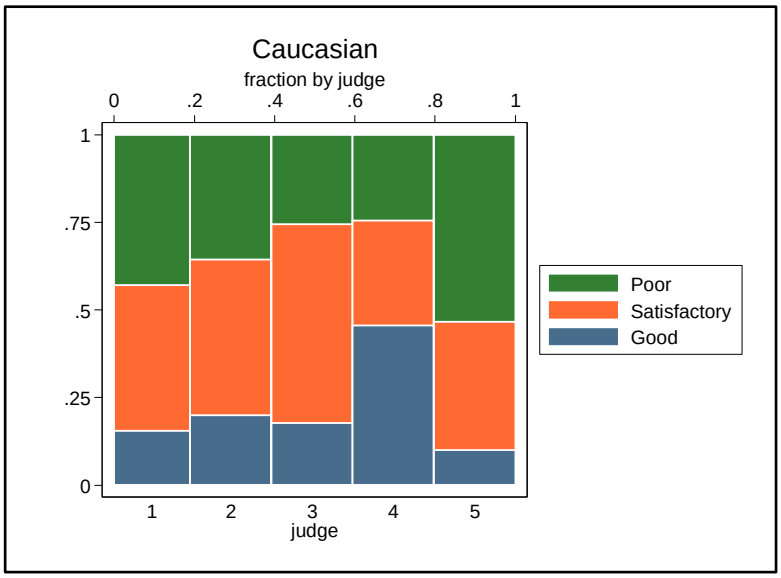


Fig. 5.19: Spine plot of judges and scores for the Caucasian data.

The area of each tile is proportional to the count for each combination of judge and score.

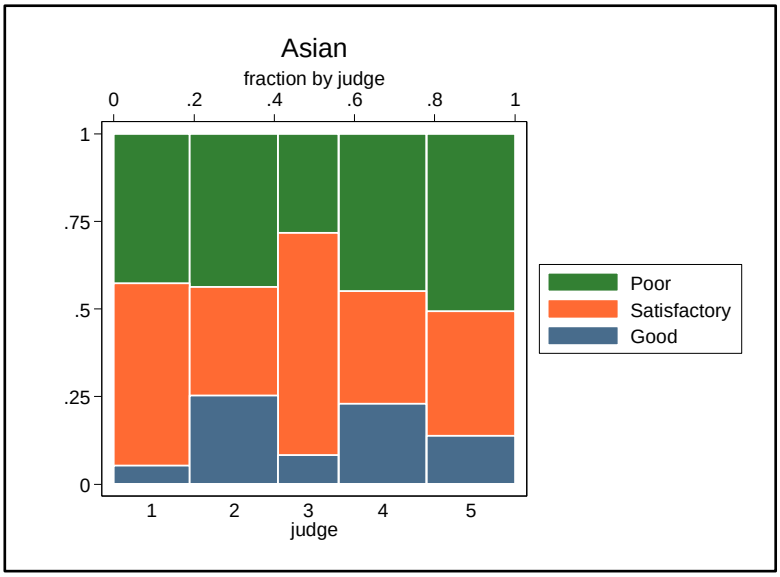


Fig. 5.20: Spine plot of judges and scores for the Asian data.

The area of each tile is proportional to the count for each combination of judge and score.

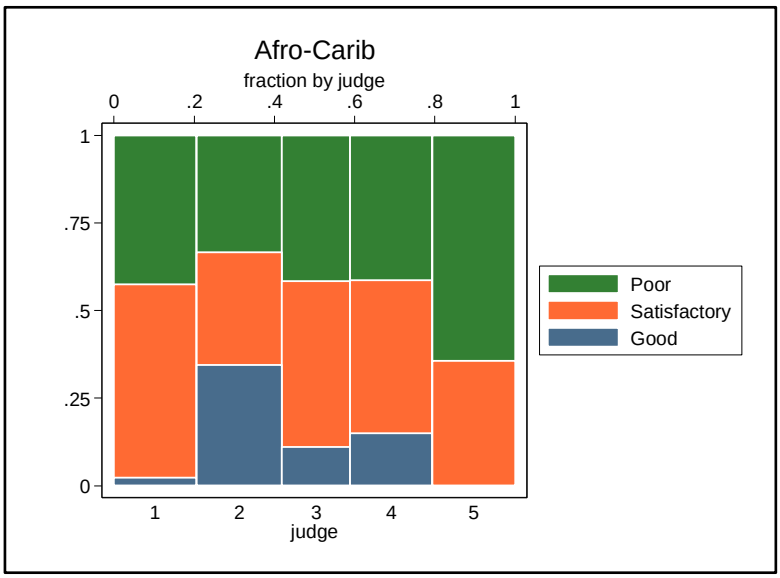


Fig. 5.21: Spine plot of judges and scores for the Afro-Carib data.

The area of each tile is proportional to the count for each combination of judge and score.

5.4. Discussion

Fabrication of an aesthetically pleasing maxillofacial prosthesis which will match with a patient's adjacent natural skin represents a challenge to the clinician and requires experience, talent and skills in order to accomplish this difficult task well. It has been stated that even if the shape and surface texture of a facial prosthesis do not perfectly replicate the anatomical structures of the defect and the appearance of natural human skin, the prosthesis is still likely to remain undetectable at a certain distance if its colour match with the surrounding skin is acceptable (Andres *et al.* 1992; Thomas 2006).

The purpose of this part of the study was to establish whether the use of a computerised colour formulation system, Spectromatch Pro, would improve the results of skin colour matching when compared with the traditional method of trial and error; and based on the results of this study, it was shown that colour matching utilising colour formulation software achieved better colour matching results when compared with the traditional method. Accordingly, we reject the null hypothesis. Furthermore, it was shown that there was a difference in skin colour measurements when using the spectrophotometer and colorimeter; we fail to reject the null hypothesis for this part of investigations.

5.4.1. Comparison of spectral instruments

Spectrophotometers and colorimeters have been frequently used for colour measurement in medical applications; and in maxillofacial prosthetic reconstruction in particular, the above have been utilised in the process of skin colour matching as well as for measurement of colour differences when investigating colour changes of maxillofacial elastomers (Al-Harbi *et al*. 2015; Bellini 2014; Coward *et al*. 2008; Hatamleh and Watts 2010[a]; Nacher-Garcia 2014; Willett and Beatty 2015).

A spectrophotometer was used as the 'gold' standard in this study for instrumental colour measurement as it provides a detailed, wavelength by wavelength spectral analysis of reflectance and/or transmission properties of objects. However, application of a colorimeter was also investigated in this study; these are recommended instruments for colour quality control, are defined as instruments for psychophysical analysis of colour as it provides measurements that correlate with the human eye-brain perception of colour (Berns 2000). They have further been used when measuring colour and colour differences in investigations in the field of maxillofacial prosthetics (Hatamleh and Watts 2010[a]; Over *et al.* 1998).

In this current study, spectral skin measurements in form of L*a*b* values were obtained utilising the spectrophotometer and colorimeter at two different times and it was shown that the above varied. Measurements with the spectrophotometer for all ethnic groups at two different times obtained L* values ranging from 37.14 to 72.63, a* values from 2.74 to 11.62 and b* values from 8.83 to 21.98. For the colorimeter, the L* values ranged from 36.84 to 73.19, a* values from 2.73 to 11.56 and b* values from 8.27 to 21.77.

Statistical analysis showed that overall there was a statistically significant difference between colour measurements taken with the spectrophotometer and colorimeter; and the hypothesis was rejected for this part of investigations. However, when looking at the L*a*b* values per ethnic group there were some statistically significant and non-significant observations. For Caucasian skin, L*a*b* were significant at t_1 but L* and b* values were non-significant at t_2. For the Asian ethnic group, all colour components were non-significant apart from the L* value at t_1. For the Afro/Afro-Caribbean group, there was only a significant difference for the L* value at t_1.

Measurement of L*a*b* values in this part of the study allowed to calculate colour differences between both instruments utilising the CIE LAB colour difference formula (ASTM 1989). A $\overline{\Delta E}$ value of 0.71 was calculated between instruments at t_1 and of 0.75 at t_2. Based on these calculated colour changes, there

was no statistically significant difference between spectrophotometer and colorimeter readings.

The use of calculated colour differences, in this part of the study between the spectrophotometer and colorimeter, inevitably involves discussion of PT and AT of colour differences. Kuehni and Marcus (1979) found that a ΔE of 1 was detectable by 50% of observers; and in 1989, Seghi *et al.* stated that a ΔE of 1 represents a colour difference that is detectable/perceivable for the average dental observer group. They further stated that sample pairs producing a measured colour difference value greater than 2 ΔE were correctly judged by the observer group 100% of the time.

Based on these findings, a ΔE of less than 1 unit, as it was calculated between spectrophotometer and colorimeter measurements in this part of the study, was below the PT stated by Kuehni and Marcus (1979) and would be unlikely detectable. In the field of body prosthetics, Leow *et al*. (2006) presented a study on PT and AT of silicone finger prostheses for patients with fair and dark skin using a colour scaling method. Based on a visual assessment using ninety observers with normal colour vision and three defined scores, the PT and AT were determined as 0.8 ΔE and 1.8 ΔE for the fair shaded silicone finger prostheses and 1.3 ΔE and 2.6 ΔE for the dark shaded prostheses, respectively.

Paravina *et al.* (2009) carried out research on colour difference thresholds of maxillofacial skin replications and stated a PT and AT for fair and dark coloured silicone specimens with 1.1 and 3.0 ΔE and 1.6 and 4.4 ΔE, respectively. Considering these reported PT and AT thresholds, the ΔE smaller than 1 unit as calculated between the spectrophotometer and colorimeter in this part of the study showed that close and unlikely detectable colour differences were observed and suggests that both instruments would be suitable for measurement of skin colour.

Nacher-Garcia (2014) conducted research on the repeatability of spectrophotometer measurements when recording the colour of human skin. The author measured spectral data of eight subject’s facial skin at the glabella using a

hand-held spectrophotometer (CM-2300d; Konica Minolta) and stated a $\overline{\Delta E}$ below 1 unit when comparing each skin scan with the mean of the subject's scans, apart from one subject with a $\overline{\Delta E}$ of 1.43. Considering the PT of 1 and AT of 2 ΔE in this current study, the latter colour difference result would be visually perceptible but clinically acceptable. However, the author concluded that spectral skin measurements recorded with the spectrophotometer were reproducible and the instrument therefore suitable to be used when recording the spectral data of skin in the field of maxillofacial prosthetic rehabilitation.

Bellini (2014) conducted research on the comparison of skin colour readings measured with a spectrophotometer (CM-2600d; Konica Minolta) and a spectro-colorimeter (E-skin; Spectromatch) for three different ethnic groups and reported a statistically significant difference between both insruments with a $\overline{\Delta E}$ of 3.45. The spectrophotometer and colorimeter utilised in this current study achieved colour differences of 0.71 and 0.75 ΔE when measured at two different times and was considerably lower than the colour changes observed by Bellini. As the same spectrophotometer was used in both studies, it can be suggested that the colorimeter achieved closer colour reading results with the spectrophotometer than did the spectro-colorimeter in the study by Bellini.

However, at this point of the study it is impossible to state whether the spectrophotometer does achieve more precise skin colour measurements to be implemented with the colour formulation software and consequently lead to closer colour matching results between elastomer and skin. Another part of this study addresses the use of recorded spectral data with the spectrophotometer and colorimeter when producing skin coloured silicone samples. Their colour assessment will be discussed at a later stage of this study and may allow any conclusion as to whether one of the utilised instruments achieves superior colour matching results.

5.4.2. Influence of time on skin colour measurements

It is aimed to establish a good colour match between the prosthesis and surrounding natural skin when fabricating maxillofacial prostheses and a successful colour match is achieved when the 'colour static' prosthesis blends at all times with the always changing, 'dynamic' colour of skin. However, the colour matching process represents one specific time or appointment during the entire manufacturing process of a maxillofacial prosthesis and generally, several weeks will pass until fabrication of a facial prosthesis will be completed (Thomas 2006).

Skin colour measurements were obtained with both spectral instruments at two times, (t_1) at the time of traditional skin colour matching and (t_2) when visual skin colour assessment was performed. A $\overline{\Delta E}$ of 2.0 was calculated for the spectrophotometer and of 1.85 for the colorimeter between t_1 and t_2. Though statistically not significant, these colour changes would be considered as visually perceptible and just acceptable differences in colour.

The colour matching process of silicone elastomer with natural skin represents a big challenge in itself and becomes even more problematic considering the consistently dynamic of human skin colour. Edwards and Duntley (1939) described skin as '…a series of different layers, each of which reflects a portion of impinging light after absorbing a certain amount at those wavelengths which are susceptible to absorption by the pigments which lie in the layer'. The main chromophores located within the different layers of skin absorb light at specific wavelengths which largely contributes to the colour of skin that we perceive (Anderson and Parrish 1981; Edwards and Duntley 1939; Findlay 1970; Young 1997).

Light absorption of melanin chromophores directly influences the skin colour in terms of tanning. A person with a fair skin colour is more likely to change skin colour when exposed to sunlight when compared to a person with darker skin. General physical health also plays an important role as low blood pressure for

example may result in a paler skin appearance and high blood pressure in a more reddish skin and this effect requires careful consideration and interpretation. A patient who considerably changes skin colour when exposed to sunlight should be advised to avoid light exposure as it may result in a visible colour difference between the prosthesis and natural skin (Thomas 2006).

The visually perceptible (1.85 ΔE) and just non-acceptable (2.0 ΔE) skin colour differences observed at two different times are likely to be related to the dynamic of skin colour. The study on the assessment of colour match between skin coloured silicone and natural skin commenced in August 2012 and was not completed until March 2013. The elapsed time between the first and second skin colour measurement for subjects ranged from 7 to 94 days and was related to availability of instrument operator and subjects at t_1 and availability of instrument operator, subjects and judges at t_2.

In maxillofacial clinical practice, it would be recommended to keep the elapsed time between colour matching and or colour measurement and prosthesis fitting at a minimum, especially avoiding any seasonal changes, when considering the effect of sunlight on skin. In this current study, subjects were asked to protect and cover the area of skin where skin colour measurements were taken to avoid any influence of skin tanning.

Nevertheless, in this current study, short and long time spans both resulted in small as well as large observed colour differences. Within the Caucasian skin colour group for example, after only 21days between the two different skin colour measurements a ΔE of 7.32 and 7.15 were recorded using the spectrophotometer and colorimeter, respectively. Another example involved a long time period of 91 days and resulted in colour differences of only 0.74 and 0.47 ΔE, respectively. For the first example, both colour measurements and colour assessment were performed in late summer and skin tanning due to sunlight exposure may have resulted in the observed large colour difference. In case of the second above mentioned example, both colour measurements and colour assessment were

undertaken in winter and reduced sunlight exposure may have been the reason for the very small recorded colour differences.

Similar observations were made for the Asian and Afro/Afro-Caribbean skin colour groups. In the latter skin colour group, after 78 days in late summer/early autumn (August – mid October) a colour difference of 6.06 and 4.57 ΔE were observed for spectrophotometer and colorimeter measurements, respectively; whereas only 0.52 ΔE were recorded for both instruments within nearly the same time period. Darker skin by nature should not be affected much in terms of tanning, hence the observed high skin colour differences may be the result of a different cause.

5.4.3. Operator influence on colour measurements

General physical health and seasonal changes have been highlighted as possible causes for observed different skin colour measurements; however, colour differences may be as well related to instrument operator practice. Both spectral instruments utilised in the current study were hand-held devices, which means the operator was lightly pressing the measuring aperture head against the skin without blanching it when recording the spectral measurements.

Piérard (1998) highlighted that the size and weight of the spectral instrument may affect the colour measurements as the lack of control of skin surface pressure by the measuring device may influence the level of compression of blood vessels which introduces a bias in the data. This measuring technique may require some practice to be performed correctly. However, the instrument operator in this study was experienced and familiar with the method of skin colour recording. Nevertheless, four skin readings were obtained per subject in this study and only accepted if within a colour difference tolerance of 0.5 ΔE.

Gozalo-Diaz *et al.* (2007) conducted research on the application of a spectroradiometer (PR 705; Photo Research Inc, Chatsworth, CA, USA) using a 0° observer and 45° illuminant optical configuration when recording spectral skin

colour data of subjects of different ethnic background. The authors stated no significant differences between the L*a*b* values for the investigated six craniofacial structures and an above satisfactory validity with regards to the calculated $\overline{\Delta E}$ of 1.46 for the twenty two measured and compared skin areas.

Bicchierini *et al.* (2005) performed investigations on the application of various systems that measure the colour of human skin. Amongst these systems were a portable contact spectrophotometer and contactless systems including a digital camera, combination of scanner and spectrophotometer and an Imaging Colour Analyser Module (ICAM). The authors reported good colour measurement and repeatability results with the traditional contact spectrophotometer with $\overline{\Delta E} < 4$; and good repeatability with a $\overline{\Delta E} < 5$ units for the contactless ICAM system. However, Bicchierini *et al.* emphasised on the good quality and system price relationship of the traditional contact spectrophotometer in comparison to the high cost of the ICAM system (> $15.000).

5.4.4. Colour match between skin and skin coloured silicone specimens

The traditional trial and erorr approach is still the most frequently used method of colour matching (Coward *et al.* 2008; Seelaus *et al.* 2011; Thomas 2006; Troppmann *et al*. 1996). However, attempts have been made in order to develop a means of quantifying pigment formulas when manufacturing maxillofacial appliances and resulted in the development of colour shade guides (Aina *et al*. 1978; Duncan and Rommerdale 1980; Guttal *et al*. 2009; Over *et al*. 1998). Nevertheless, improved systems were needed that also control the phenomenon of metamerism, which refers to a match or mismatch of two colours when viewed under varying lighting conditions.

Troppmann *et al.* (1996) were the first to describe the application of a computerised colour formulation software paired with spectrophotometry in order to establish a silicone skin colour base shade. Utilising this scientific approach, Spectromatch Pro was developed and is currently the only readily available colour formulation software of its kind for maxillofacial prosthetic use. In this

part of the study, skin coloured silicone samples were manufactured based on colour matching following a) the traditional method and b) utilising computerised colour formulation software, Spectromatch Pro. When applying the latter method, the recorded L*a*b* values of subject's skin were used to generate individual skin colour recipes.

The results of this part of the study showed that there was a statistically significant effect of samples manufactured based on the traditional colour matching method and those made utilising Spectromatch Pro ($p = 0.001$). Furthermore, there was a statistically significant interaction between manufactured silicone samples and ethnic group with regards to the two different times of colour measurement.

5.4.4.1. Traditional colour matching method

It can be stated that skin coloured silicone samples whose manufacture was based on traditional colour matching resulted in highest colour differences when compared with original skin colour readings at t_1. Maximum colour differences of 4.88 $\overline{\Delta E}$ were observed for the Afro/Afro-Caribbean skin tone, followed by 4.05 $\overline{\Delta E}$ for Asians and lowest values were calculated for the Caucasian skin type with 3.46 $\overline{\Delta E}$. These results highlight again that traditional colour matching is governed by three main contributing factors and include lighting conditions, the appearance of skin to be colour matched and the skills of the clinician undertaking the colour matching procedure (Coward *et al*. 2008; Seelaus *et al.* 2011; Thomas 2006; Troppmann *et al.* 1996).

In terms of lighting conditions, the clinician needs to consider two general principles when undertaking traditional skin colour matching and involves that the type and level of illumination should mimic as closely as possible that under which the facial prosthesis will be viewed (Berns 2000; Hunt and Pointer 2011). When considering the object of colour matching, which is in this particular case the natural living skin, the patient's skin colour needs to be of 'normal' appearance, with no effects of skin tanning, should demonstrate 'normal' blood

circulation and no presence of any other skin blemishes that could affect the outcome of traditional skin colour matching (Coward *et al.* 2008; Thomas 2006). The subjective effect on colour matching utilising the traditional method is dependent on the clinician undertaking the colour matching procedure. As mentioned before, artistic talent and expertise are undoubtedly the most influencing factors on the colour matching outcome; however, fatigue may not be underestimated. Even the most talented and experienced clinician may struggle to produce a good colour match if generally unwell or just simply tired.

The greatest colour differences of 4.88 $\overline{\Delta E}$ were observed for Afro/Afro-Caribbean skin tones and smallest for Caucasians with 3.46 $\overline{\Delta E}$. This is in agreement with the general perception that colour matching Asian and Afro/Afro-Caribbean skin tones may become a challenge, especially if the clinician predominantly treats Caucasian patients; this is based on the fact that the clinician will be more adept at recognising the skin tones of patients he treats regularly (Thomas 2006). Such darker skin tones appear to have a more subtle depth and it can be difficult to mix the correct tone. The investigator in this current study has mainly treated patients of Caucasian ethnic background; hence, the observed colour matching results of this study agree with the statement by Thomas.

The above mentioned many variables involved in this process can make the traditional colour matching method time consuming and its results unpredictable (Troppmann *et al*. 1996). It can further be stated that the spectral reflectance curves of these samples were more dissimilar to the spectral curves of the corresponding natural skin than those of samples based on colour formulation software. Gillman (1951) tried to match the spectral curves of human skin pigments with those of pigments used in facial prosthetics and described the potential to reduce the effect of metamerism by approximating the spectral curves of pigments with those of natural skin.

In 1969, Cantor *et al.* already appreciated that application of spectrophotometry enables professionals to analyse and measure the appearance of skin through measuring of its spectral reflectance curve. A spectral reflectance curve

represents how objects, which are in maxillofacial prosthetic practice the natural skin of a patient and the facial prosthesis, reflect the incoming light within the visible spectrum of light; and the more approximate these spectral curves are the more similar is their response to light and in turn their colour. Two spectral reflectance curves from the obtained spectral data of subjects are shown in Figs. 5.22 and 5.23; and these represent the spectral data of the smallest and largest calculated colour differences between a subjects' skin colour measurement and the corresponding manufactured skin coloured silicone sample using the traditional colour matching method. The graphs shown have been taken directly from the 'Colour Compare' software provided by Spectromatch Ltd .

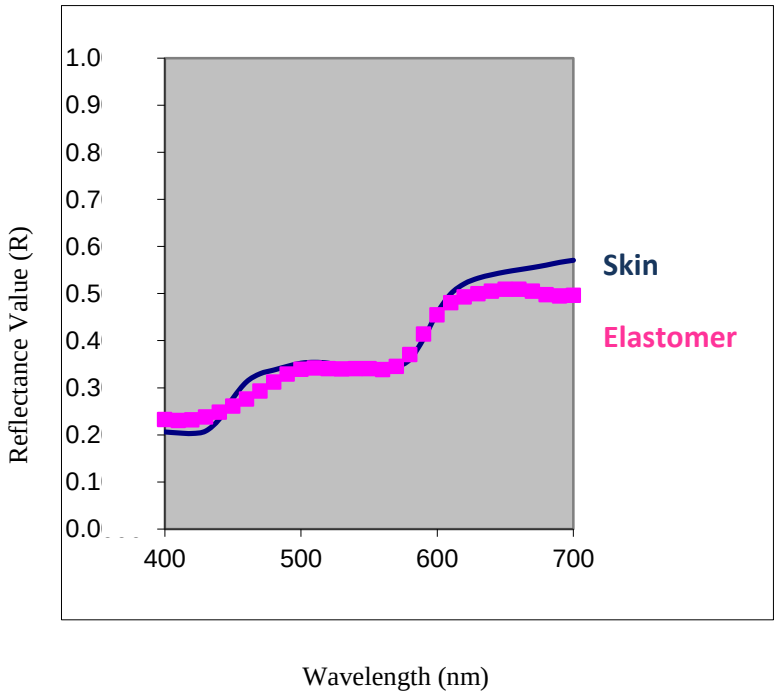


Fig. 5.22: Spectral reflectance curves for smallest colour differences between skin and corresponding silicone sample (Caucasian skin tone).

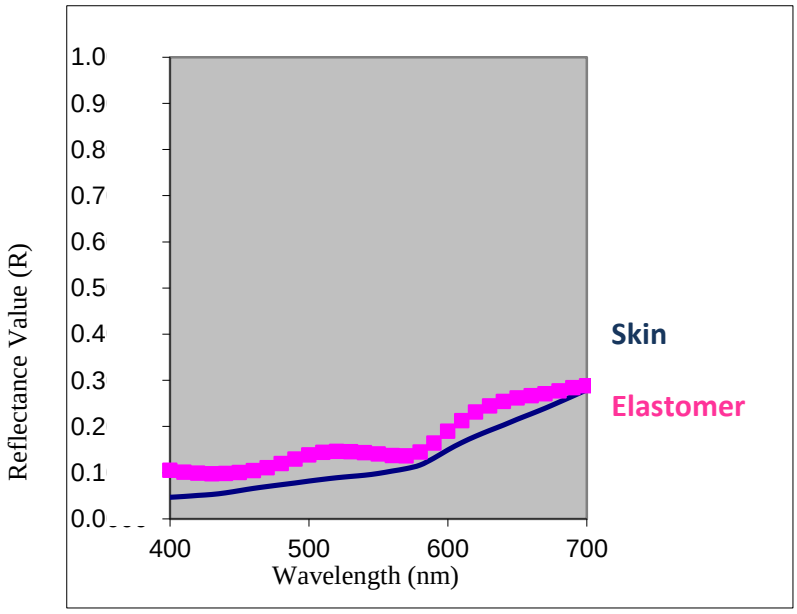


Fig. 5.23: Spectral reflectance curves for largest colour differences between skin and corresponding silicone sample (Afro/Afro-Caribbean skin tone).

In summary, traditional skin colour matching represents a non-scientific and subjective method with a small likelihood of achieving similar spectral reflectance curves and in turn similar colours between natural skin and a maxillofacial prosthesis. Furthermore, the effect of metamerism cannot be controlled without utilising a scientific approach in the form of spectrophotometry (Coward *et al.* 2008; Troppmann *et al*. 1996).

5.4.4.2. Colour matching based on colour formulation software

Based on the results of this part of the study, when comparing skin coloured silicone samples with the original skin colour recordings, the samples manufactured based on spectrophotometer readings produced best colour matches in comparison to samples based on colorimeter readings and the traditional method of colour matching. From the skin coloured samples based on spectrophotometer readings, greatest colour differences of 1.46 $\overline{\Delta E}$ were obtained for the Caucasian skin tone, followed by Asians with 1.13 $\overline{\Delta E}$; lowest values were calculated for the Afro/Afro-Caribbean skin type with 0.79 $\overline{\Delta E}$. Analysis of data

showed statistically significant effects of the colour matching method ($p = 0.001$) and no effect of ethnic groups. However, Šídák's multiple comparisons of means test demonstrated only statistically significant difference between skin colour measurements and samples based on the traditional colour matching method.

The observed results generally demonstrated that colour matching based on colour formulation achieved superior results when compared with the tradiational trial and error method. Utilising this approach, the many variables involved with the trial and error method are excluded and the previously subjective method has been replaced with an objective, scientific method that uses spectral colour measurement and also controls the phenomenon of metamerism.

The need for predictable, precise as well as repeatable colour matching systems in the field of maxillofacial prosthetsics has been long recognised (Aina *et al.* 1978; Cantor *et al.* 1969; Over *et al*. 1998; Troppmann *et al*. 1996). Troppmann *et al.* (1996) described the application of a computerised colour formulation software paired with spectrophotometry (both Hunter Associates Laboratories Inc., Reston, Virginia, USA) in order to establish a silicone elastomer skin colour base shade for subjects of Caucasian skin type. The authors used for their study four ferro silicone paste pigments and A-2186 elastomer (Factor II); and the colour formulation process was based on an iterative procedure where the colour differences between elastomer and natural skin were decreased with successive skin colour formula corrections aiming to approximate the spectral curves of a subject's skin colour and the silicone elastomer and achieved final colour differences ranging from 2.25 to 3.33 $\overline{\Delta E}$.

Since then, Coward *et al.* (2008) have investigated the use of computerised colour formulation software in a pilot study to colour match the skin colour for African-Canadian subjects. The authors used a technique similar to that described by Troppmann *et al.* (1996); however, nine instead of four different pigment pastes were utilised. Based on iterative colour corrections, the authors achieved colour differences for the final silicone specimen (swatch 4) of 19 subjects ranging between 1.49 to 8.82 $\overline{\Delta E}$. It was stated that only one of the 19 subjects recorded a

$\overline{\Delta E}$ value lower than 2 units. However, the results further showed that the $\overline{\Delta E}$ between skin coloured silicone samples decreased with each iteartive mix ($\overline{\Delta E}$ swatches 1 – 2 = 3.20; $\overline{\Delta E}$ swatches 3 – 4 = 1.01). The authors concluded that the colour formulation system produced similar colour matching results to that conducted by Troppmann *et al.* (1996).

Similar colour differences were also observed for the Afro/Afro-Caribbean ethnic group in this current study with 0.79 $\overline{\Delta E}$ for silicone samples based on spectrophotometer readings and 1.01 $\overline{\Delta E}$ for samples based on skin colour readings obtained using the colorimeter. These results demonstrate that colour formulation software combined with instrumental skin colour measurement can achieve colour differences around and below the visual PT of 1 ΔE for specific ethnic groups. However, Coward *et al.* (2008) also emphasised that further research is needed, in particular to investigate the level of translucency of coloured silicone elastomer in comparison to natural skin.

In a recent study, Nacher-Garcia (2014) investigated the pigment formulae reproducibility of Spectromatch Pro utilising pigment premixes, which is the latest available version of the colour formulation software. These pigment premixes are lower concentrated elastomer/pigment colourants and require a lower weighing tolerance of 0.1 g in comparison to the high concentrated pigment pastes applied in this current study which makes a direct comparison of both studies impossible.

Nacher-Garcia (2014) obtained $\overline{\Delta E}$ of 0.82 and 0.69 for the white ethnic group, 0.73 and 1.07 for Chinese, 0.92 and 0.43 for Asian and 0.81 and 1.36 for the Black ethnic group. These colour difference values were lower than the colour differences observed between original skin spectral data and manufactured skin coloured silicone samples in the current study with $\overline{\Delta E}$ of 1.45 for the Caucasian skin colour type, 1.12 for Asian and 0.78 for Afro/Afro-Caribbean. However the results of both studies cannot be compared directly as Nacher-Garcia used a different colourant system and 2 subjects per ethnic group (total of 8 subjects) whereas 30 subjects (total of 90 subjects) were used in this current study.

For the Caucasian ethnic group in this current study, 50% of subjects demonstrated a $\overline{\Delta E}$ below the PT of 1 and for only 5 subjects a $\overline{\Delta E}$ of more than 2 was calculated. The Afro/Afro-Caribbean ethnic group achieved lowest colour differences with a $\overline{\Delta E}$ below 1 for 20 subjects and none above the AT of 2. Furthermore, Nacher-Garcia applied the ΔE CMC for colour difference calculations, whereas the CIE L*a*b* colour difference formula (ASTM 1989) was utilised in the current study.

However, it may be argued that a sample size of two subjects is too small to draw any substantial conclusions on the colour match between natural skin and manufactured silicone samples as applied by Nacher-Garcia (2014). The author has taken 6 skin colour readings per subject of the same location (glabella) at five minutes intervals between colour readings which is rather a repeatability test of measurements than an objective approach to assess the colour match between natural skin and skin coloured silicone elastomer. In this current study, four skin measurements were recorded with a 10 mm distance between measuring points on the left supine forearm, all within a colour difference tolerance of 0.5 ΔE, and subsequently averaged to obtain one skin colour reading per subject. Utilising this approach, the colour match between natural skin and skin coloured silicone elastomer for a much wider variation of skin nuances within each of three ethnic groups could be investigated. The overall colour difference between skin and silicone elastomer samples for 90 subjects was 0.79 $\overline{\Delta E}$ and demonstrated very good colour matching results using the Spectromatch Pro colour formulation software.

The spectral reflectance curves for the best colour match between skin and skin coloured elastomer based on colour formulation software is shown in Fig. 5.24 and demonstrates the importance of approximation of spectral curves in order to achieve a close colour match.

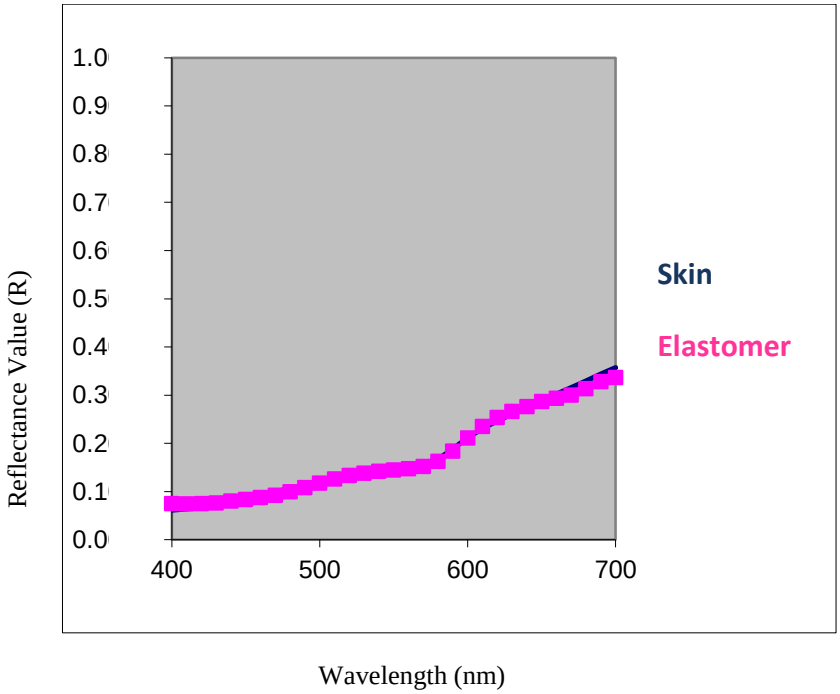


Fig. 5.24: Spectral reflectance curves for smallest colour difference between skin and corresponding silicone sample (Afro/Afro-Caribbean skin tone).

5.4.5. Colour match between skin and skin coloured samples with regards to PT and AT

A PT of 1 and AT of 2 ΔE was, as previously discussed, applied in this current study. Statistical analysis of the effect of PT and AT in relation to colour matching method and ethnic group showed that there was a statistically significant effect ($p = 0.001$) of colour matching method on both, PT and AT; however, ther was no significant effect of ethnic group.

The results revealed that from a total of 270 elastomer samples 92 samples demonstrated colour differences below the PT of 1 ΔE. However, when considering the AT, 171 samples of the 270 were below the AT of 2 ΔE and represented clinically acceptable colour matching results. When considering ethnic groups, Caucasian skin coloured samples demonstrated worst colour matches with only 26 from 90 samples below the PT and 53 from 90 below the AT. Best colour matches were observed for the Afro/Afro-Caribbean group with

37 from 90 samples below the PT and 61 from 90 samples below the AT, meaning more than two thirds of these samples demonstrated clinically acceptable colour matching results.

These results support again the observation that Afro/Afro-Caribbean skin coloured silicone samples demonstrated best colour matching results in conjunction with the colour formulation software; and that in general the application of colour formulation software obtained superior colour matching results when compared with the traditional method. The vast majority of samples manufactured based on Spectromatch Pro achieved clinically acceptable colour matching results whereas for the traditional trial and error method, only 11 from 90 samples were below the AT of 2 ΔE. Summarising, it can be stated that application of colour formulation software does achieve better colour matching results than the traditional method and is in agreement with the literature (Coward *et al*. 2008; Nacher-Garcia 2014; Seelaus *et al.* 2011; Troppmann *et al.* 1996).

5.4.6. Visual assessment of colour match

The results obtained based on instrumental colour match assessment in the previous section showed that colour formulation achieved more consistent, more precise and more reliable colour matching results than did the traditional chair side colour matching method. However, in clinical practice of maxillofacial prosthetics, the final judgement of colour match or mismatch between the prosthesis and surrounding natural skin will be carried out by the clinician and the patient. Therefore, the second part of investigations of this part of the study involved a visual comparison of skin coloured silicone samples, which were manufactured based on traditional colour matching and colour matching utilising Spectromatch Pro, in comparison with natural skin.

Generally, based on the instrumental measurements of colour, the subsequently calculated colour differences should reflect what observers see. For this particular application, the calculated colour differences between skin and manufactured silicone samples should demonstrate a good colour match when assessed by an

observer as the majority of samples demonstrated $\overline{\Delta E}$ values within the clinical AT when the colour of samples was measured with the spectrophotometer.

In this current study, the degree of colour match was assessed by five judges who gave a score on the colour match between 1 (very good) to 5 (poor); however, for statistical analysis 3 condensed scores were used (good, satisfactory and poor). The results showed that there was a statistically significant effect of colour matching method, judge, and the interactions of colour matching method and judge, as well as judge and ethnic group ($p = 0.001$). However, there was no statistically significant effect of ethnic group as a main factor ($p = 0.134$). Šídák's multiple comparisons of means test showed that the traditional method of colour matching was statistically significantly different from colour formulation software. Furthermore, judges 2, 3 and 4 were not significantly different but there was a statistically significant difference of judges 1 and 5. Šídák's multiple comparisons of means test was applied when comparing judge, colour matching method as well as judge and ethnic group; and considering these interactions, no obvious pattern was detected.

A total of 270 skin coloured silicone samples were assessed and the five assessors provided 1263 scores; of which 214 scores were a 'good' colour match and 520 considered as 'poor' (Fig. 5.25). The number of scores judges have provided is different between them as not all judges as well as subjects were present for all scheduled visual colour assessments.

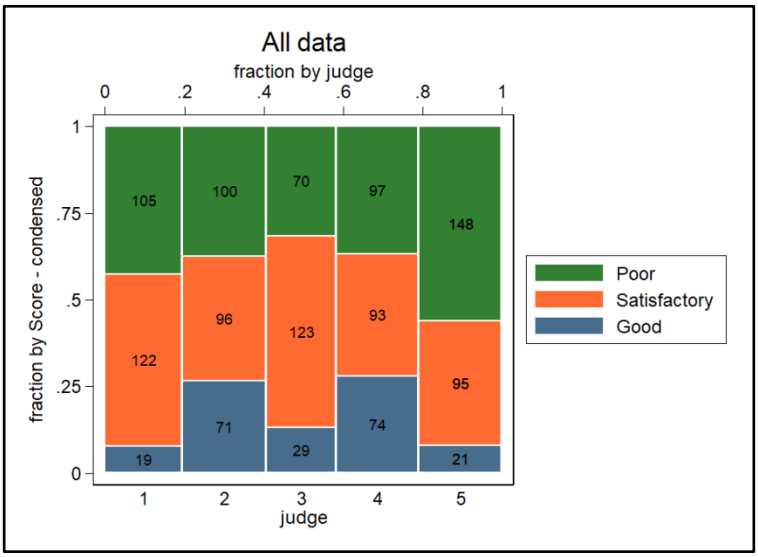


Fig. 5.25: Spine plot of judges and the scores for the combined data.

The area of each tile is proportional to the count for each combination of judge and score.

When condensing these results by combining ‘good’ and ‘satisfactory’ scores, and these were also considered as clinically acceptable colour matching results, than 58.83% of all samples were clinically acceptable. When including the results with regards to the AT, based on instrumental colour match assessment, 171 samples from a total of 270 samples were within the AT of 2 ΔE which is the equivalent to 63.33%. This shows that the overall scores results of visual colour assessment were not too dissimilar from the calculated colour differences, considering the condensed good and satisfactory scores were acceptable colour matching results.

The literature on visual colour assessment between natural skin and skin coloured silicone samples is very limited. Seelaus *et al.* (2011) performed visual assessment of colour match between skin and skin coloured silicone samples for 19 African-Canadian subjects. The authors utilised colour formulation software in order to produce a skin base shade and performed four iterative correction mixes of individual skin colour recipes. Five judges performed visual colour assessment and the results showed that sample 1 for each subject was rated a worse match

than the last iterative mix, sample 4 ($p<0.015$). This was in agreement with the previously calculated colour differences for these iterative colour mixes from the first part of this study (Coward *et al*. 2008) and is in agreement with the observations made in this current study.

From the five colour match assessors used in this current study, three were experienced clinicians in maxillofacial prosthetic rehabilitation (judges 1, 3, 5) and two were lay persons (judges 2, 4). Furthermore, two of the clinicians (judges 1, 5) have been working together treating patients for more than 15 years; however, these judges were significantly different when giving scores on colour matches in this part of investigations. This again demonstrates the variability of human colour perception. Alterations in colour perception can occur as a result of uncontrolled factors including fatigue, emotions, ageing, lighting conditions and metamerism; and different visual sensitivity to colour highlights the subjectivity of visual colour assessment (Berns 2000; Hunter 1987; Seghi *et al.* 1989). Seelaus *et al.* (2011) analysed the intra- and inter-judge reliability and stated that judges were consistent with their scores when assessing a silicone sample for the second time but there was a considerable variability among judges' scores of the same sample. This observation is in agreement with the current study where no obvious pattern was found in judges' scores.

The only other study identified on visual colour assessment between skin and manufactured silicone samples was conducted by Bellini (2014) where the author investigated the application of a recently introduced colour formulation system for maxillofacial applications, namely E-skin (Spectromatch), utilising a spectro-colorimeter. This system offers the clinician also the opportunity to add fibre flocking to a skin colour recipe. The author carried out visual colour assessments of silicone elastomer samples, with and without flocking. From the 336 silicone sample assessments, 19 were considered as 'good' colour matches, 155 samples as 'satisfactory', 150 'unsatisfactory' and 12 'poor'. For the samples considered as 'good' and 'satisfactory', the majority of specimens contained flock in contrast to the 'unsatisfactory' group where the majority were without flock. However, the agreement of judges' scores when assessing the silicone samples against the skin

area was low (38.39%). The author stated that even though the three judges were experts in the field of maxillofacial prosthetics, there were still differences in their experience, visual sensitivity and possibly even their objectivity; and this was in agreement with the observations made in this current study.

The study by Paravina *et al.* (2009) did not focus on comparison between natural skin and manufactured silicone samples; however, the authors' investigations on colour difference thresholds for maxillofacial applications highlighted the problems involved with visual assessments of colour differences. Paravina *et al.* used 45 observers to assess the colour differences of 30 pairs of silicone samples representing fair and dark skin tones in a viewing booth by rating colour differences as a 'perfect match', 'acceptable mismatch' or 'unacceptable mismatch'. The colour of silicone samples was also measured with a spectrophotometer and colour differences calculated accordingly. With regards to assessors' scores, the authors stated inconsistency as some observers stated imperfect matches for samples with a low colour difference value and perfect matches for samples with a higher colour difference. Furthermore, in some assessments observers judged all silicone specimens with the same score. To minimise these problems, judges received colour assessment training; and as a result, consensus was achieved for the vast majority of assessments with a perfect match ($\Delta E < 1$) and unacceptable mismatches ($\Delta E > 5$). This demonstrates again the problematic involved with variability of human colour perception as also observed in this current study.

It was shown that very small colour differences and larger colour differences can be correctly assessed by observers but no answer was provided with regards to intermediate colour differences. Do all of these intermediate results fall within the colour difference range for acceptable colour matches? Is there a general cut-off point for perceivable and acceptable colour differences? As frequently stated, colour perception is a very complex and subjective factor. Different perceptibility and acceptability thresholds of colour differences for maxillofacial applications have been established in the past but it is uncertain whether one of them describes an applicable and correct value. Further work is needed to better relate the

observed colour differences when comparing instrumental with visual colour assessment. From the authors' point of view, at the current time and in the field of maxillofacial prosthetic rehabilitation, the patient provides the final 'score' on a colour match or mismatch when a facial prosthesis has been finalised and fitted; and it surely represents yet another subjective judgement but has to be taken into consideration.

5.4.7. Factors influencing visual colour assessments

The light source plays an important role when assessing the colour of objects and changes in that light source may be the reason why in some cases the colour of an object can appear different, giving the sense of mismatching, known as metamerism (Berns 2000; Hunt and Pointer 2011; Hunter 1987).

A standardised viewing environment for visual colour match assessments was utilised in this study. Colour difference assessments were performed using the Q-Lab viewing booth with a D65 light source in order to perform all observations under the same lighting conditions and was in accordance with recommended conditions for visual colour assessments (Berns 2000; Hunter 1987). Commercial viewing booths for visual colour assessment investigations in the field of maxillofacial prosthetics were also utilised by Bellini (2014), Leow *et al.* (2006), Paravina *et al.* (2009) and Seelaus *et al*. (2011). Though the same lighting conditions and standardised viewing environments within the colour assessment booths were applied, a direct comparison between these studies and with the current study is not possible due to varying aims and objectives of investigations and research methodology.

In comparison to the above, Nacher-Garcia (2014) performed visual assessment of colour differences when establishing AT for maxillofacial applications without utilising standardised viewing conditions in a colour viewing booth. Colour difference assessments were carried out under D65 lighting conditions in a laboratory room. Subjects were seated in a clinical chair opposite a window with the sample to be assessed placed on the glabella; and the assessors were

positioned in line in order to perform colour difference assessments. This viewing arrangement resulted in different distances and viewing angles between observers and samples to be assessed; furthermore, the proximity to the window may have influenced the observers' scores as a result of changing light intensity during the course of the day. Hence, it is arguable that the established AT values for maxillofacial applications by Nacher-Garcia are applicable.

As previously shown, both observers and lighting conditions play an important role in visual colour difference assessments; however, the importance of the object to be assessed may not be underestimated. In this current study, the colour of two different objects was compared, namely natural skin and skin coloured silicone. Natural skin with its different layers is inherently different from silicone elastomer which is used to mimic skin in maxillofacial applications; hence, their different optical properties add to the problems encountered with colour matching natural skin with silicone elastomer.

In maxillofacial applications, pigments and fibre flocking are added to the otherwise translucent elastomer to produce a colour match between skin and silicone. However, only the right degree of translucency or opacity of the coloured elastomer will produce a life-like looking prosthesis. Aina *et al.* (1978) investigated the colouring effects of synthetic inorganic iron oxides and titanium dioxide at 1% and 0.1% by weight pigment concentrations when colour matching elastomer with natural skin for three subjects of African ethnic background. The authors realised that the use of 1% weight of black pigment completely masked the other used pigments (brown and umber) and could only overcome this problem by reducing the concentration of black to 0.1% weight or application of a smaller portion of the 1% black stock colour. It was shown that a careful selection of pigment concentration is required to achieve a translucency and opacity level that approximates those of natural skin.

Johnston *et al.* (1995) investigated the masking (opacifying) power of dry mineral earth pigments and fibre flocking dispersed in maxillofacial silicone elastomer. The authors used dry pigments at 0.1% weight and fibre flocking at 0.2% weight

for all experiments and stated intermediate opacifying power to those of other dry earth pigments. The authors agreed with the study by Aina *et al.* (1978) stating that the masking power of black and titanium white were substantially greater than those of all other investigated chromatic pigments.

Erb (1995) describes a pigment concentration for an appropriate translucency level of silicone elastomer in maxillofacial applications for subjects of Caucasian and African ethnic groups with 0.15% and 0.30% weight, respectively, whereas Troppmann *et al.* (1996) stated final pigment loading between 0.15% to 0.25% weight for the Caucasian skin type after the third and final correction elastomer mix when establishing a skin colour base shade. Seelaus and Troppmann (2000) later determined 0.16% weight of colourants as appropriate to colour match natural skin with elastomer; and Coward *et al.* (2008) reported a mean pigment loading of 0.31% weight for the final iterative silicone mix when colour matching elastomer to African-Canadian subjects, with individual pigment loading ranging from 0.20% to 1.96% weight.

The development of the Spectromatch Pro colour formulation software, which was used in this current study, is generally based on a pigment loading of maximum 0.2% weight of colourants and is in agreement with the literature (Erb 1995; Seelaus and Troppmann 2000; Troppmann *et al*. 1996).

The variety of values in terms of recommended translucency of silicone elastomer in facial prosthetics emphasises on the complexity of colour matching; this becomes again more problematic when involving besides elastomer translucency the material thickness. Over *et al*. (1998) established an intrinsic silicone shade guide for facial prostheses in form of 6-steps wedge silicone samples (1, 2, 4, 6, 8 and 10 mm thickness). As one part of this research, visual assessment was performed to assess the colour match between subjects' natural skin and the colour of fabricated step wedge silicone samples. The authors stated that all colour match assessors found that from all different step wedge samples, the samples of 6, 8 and 10 mm thickness provided the best colour match with skin. The authors suggested that lesser sample depths at the predetermined colourant

loading allowed the subjects' skin colour to show through. However, this has clinical implication as the fine margins of facial prostheses are less than 1 mm in thickness.

Nacher-Garcia (2014) produced samples of varying thickness which were visually assessed for colour match between skin and elastomer samples as part of experiments when establishing the AT for colour matching in maxillofacial prosthetics. Based on the results, the author stated that a minimum thickness of 6 mm was required for achieving a good skin - elastomer colour match with appropriate level of translucency, whereas a minimum thickness of 8 mm was reported for the African ethnic group.

Development of the Spectromatch Pro colour formulation system was in terms of translucency based on a 8mm sample thickness and was in agreement with the results obtained by Nacher-Garcia (2014) utilising this colour matching system. A sample thickness of 8 mm was chosen in this current study as this was determined as the optimum translucency in the development of the Spectromatch Pro software. However, in clinical maxillofacial practice, the periphery of a facial prosthesis will demonstrate areas with larger elastomer thickness (tip of a nasal prosthesis, helix of an auricular prosthesis or central area of an orbital appliance), whereas the fine prosthesis margins will taper towards '0' (knife edge). These fine margins are required to achieve a 'blending' of the elastomer with natural skin. The effect of translucency of a subjects' colour match between such fine margins in comparison to thicker material areas has not been investigated; and further research is needed to adjust for this in clinical practice.

5.5. Conclusion

Based on the results of instrumental and visual colour assessment of colour matches between manufactured skin coloured silicone and natural skin it can be concluded that computerised colour formulation achieved better colour matches than did the traditional method of trial and error. Furthermore, the use of a spectrophotometer for skin colour measurement resulted in best colour matching results; with lowest and non-perceivable (< 1ΔE) colour differences obtained for the African/Afro-Caribbean skin colour group. These observations provide evidence for suitability of Spectromatch Pro to be integrated in the daily clinical practice in maxillofacial prosthetic rehabilitation.

INVESTIGATIONS ON THE APPLICATION OF SILICONE SURFACE SEALANTS AND THE USE OF UV-LIGHT ABSORBERS

6.1. Introduction and aims of investigations

Colour changes of maxillofacial silicones have been frequently reported and UV-light has been identified as one its main causes (Al-Harbi *et al.* 2015; Beatty *et al.* 1995 and 1999; Gary *et al*. 2001; Haug *et al*. 1999; Hatamleh and Watts 2010[a]; Polyzois 1999). As a consequence, attempts have been made in order to improve the colour stability of maxillofacial silicones.

Research has been conducted on the intrinsic use of UV-light absorbers and light stabilisers; and whereas one study showed that none of the photo protective agents provided any significant level of UV-light protection other authors reported improved colour stability for maxillofacial elastomer (Bryant *et al.* 1994; Han *et al*. 2014; Kheur *et al.* 2016; Tran *et al.* 2004).

Silicone sealants have been traditionally used to cover and protect the extrinsic colouring and added characteristics on the surface of facial prostheses. It has been suggested that such surface sealants may protect the underlying main body of facial prostheses from adverse effects caused by extra-oral environmental factors. It was shown that application of an extrinsic surface sealant containing a high concentration of pigments protected the underlying base elastomer from discolouring when exposed to UV-light (Beatty *et al.* 1999).
Although some promising results have been reported when using UV-light absorbers and a silicone surface sealant no further research has been directed towards these applications. The aims and objectives of this part of the study involved experiments using two different silicone surface sealant techniques, involving Parylene coating and application of a commercially available silicone extrinsic sealant in combination with the use of UV-light absorbers, aiming to improve the colour stability of maxillofacial elastomer.

6.2. Materials and methods

M511 (Technovent) and Spectromatch Pro pigments (Spectromatch) were again used in this part of the study. All other new utilised materials are summarised in Table 6.1.

Material		Manufacturer
UV-light absorber	Semasorb	Se ma Gesellschaft für Innovationen mbH, Coswig, Germany
	2-hydroxy-4-methoxy-benzophenone (2H4MB)	Sigma-Aldrich Chemie GmbH, Munich, Germany
	Uvinul A Plus B	BASF SE, Ludwigshafen, Germany
Surface Sealant	Parylene HT	Specialty Coating Systems (SCS), Woking, UK
	Commercial extrinsic silicone sealant; P799	Technovent Ltd., Bridgend, UK

Table 6.1: Materials.

6.3. Study design

6.3.1. Intrinsic use of UV-light absorbers

The organic pigment Alizarin Crimson, as one of the pigments frequently used when mixing skin shades was utilised to manufacture coloured silicone test samples for investigations involving UV-light absorbers. Six test specimens were manufactured per UV-light absorber; a total of 36 test samples were subsequently stored in darkness and exposed to accelerated ageing for 1000 hours. The design of this part of investigations is shown in Fig. 6.1.

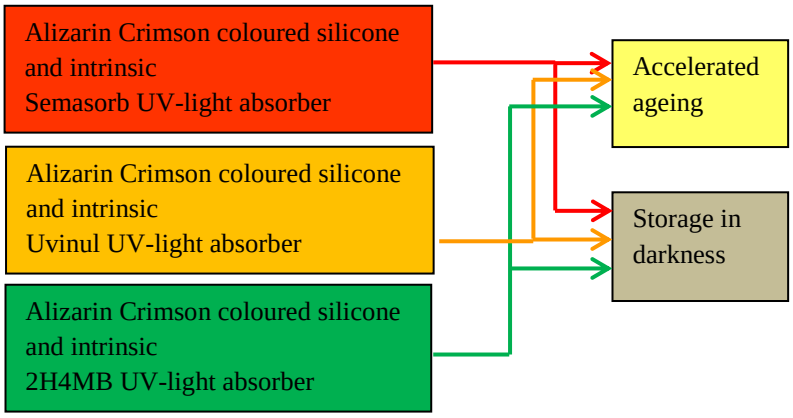


Fig. 6.1: Study design – intrinsic use of UV-light absorber.

6.3.2. Parylene surface coating, silicone mixing in nitrogen environment

For Parylene coating, Alizarin Crimson and Malachite Green coloured samples were produced and then sent to a commercial company, Specialty Coating Systems (SCS), to apply the surface coating. Furthermore, Alizarin Crimson and Malachite Green coloured silicone elastomer was mixed in a nitrogen environment before curing. All prepared test samples (Parylene coating and silicone mixing in a nitrogen environment) were subsequently stored in darkness

and exposed to accelerated ageing for a total of 1000 hours. Six samples were produced per pigment, test group and conditioning type (Fig. 6.2).

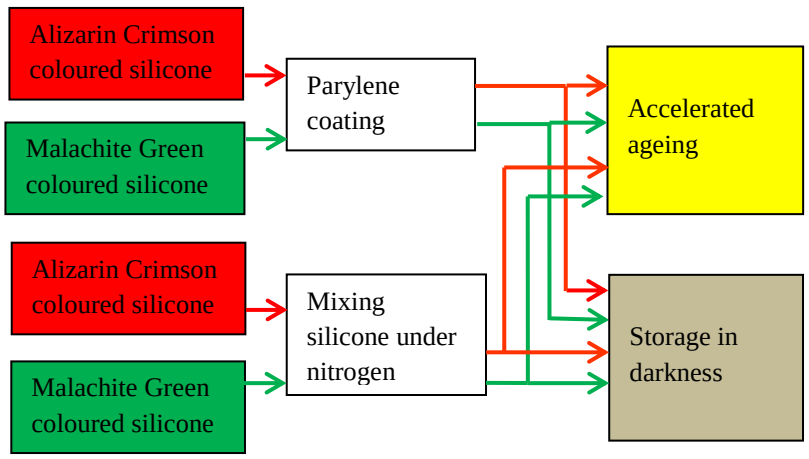


Fig. 6.2: Study design – Parylene coating and silicone mixing in nitrogen environment.

6.3.3. Incorporation of UV-light absorber into surface sealant: A pilot study

The UV-light absorber 2H4MB was used to undertake a pilot study where it was added to a commercial extrinsic silicone sealant. Two test groups were established, M511 samples with the surface sealant only and elastomer with the surface sealant containing 2H4MB. Both test groups involved non-pigmented elastomer and M511 coloured with Alizarin Crimson, Logwood Maroon, Indian Yellow and a combination of pigments to establish a Caucasian skin tone. These pigments were chosen as they are frequently used when mixing skin tones. Furthermore, they are organic pigments and demonstrated visible colour changes in previous experiments, Chapter 3. Three specimens were manufactured per pigment and test group; and they were exposed to accelerated ageing for a total of 1500 hours (Fig. 6.3).

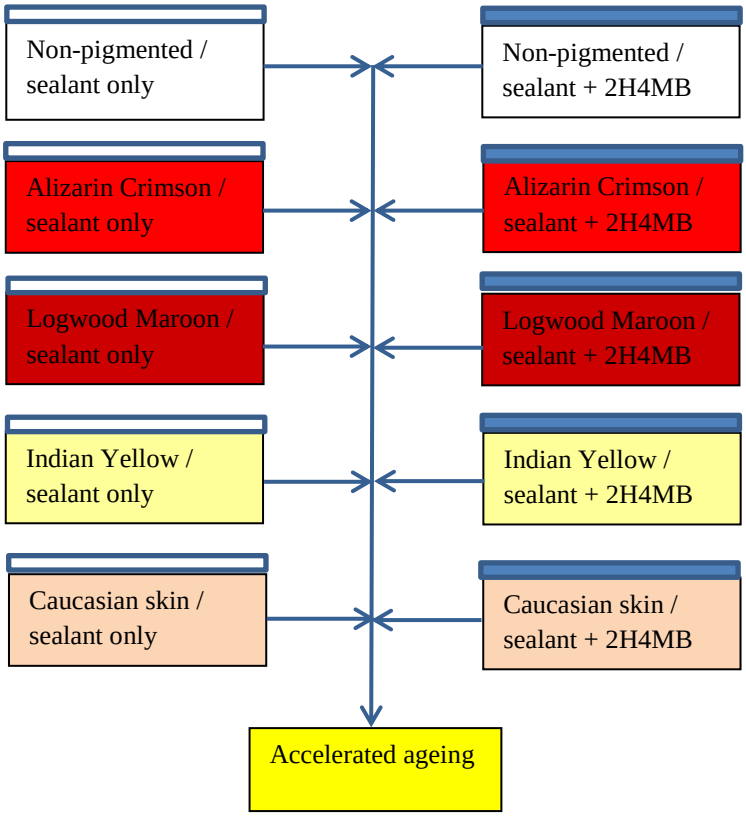


Fig. 6.3: Study design – Test samples with sealant only and sealant with UV-light absorber 2H4MB.

6.3.4. Caucasian skin coloured elastomer: no sealant compared with sealant only and sealant / UV-light absorber

Caucasian skin coloured samples without a surface sealant layer were fabricated and served as a control. Furthermore, Caucasian skin coloured samples with a sealant layer only were manufactured as well as samples with the sealant and incorporated 2H4MB UV-light absorber. Six samples were prepared per test group and subsequently exposed to accelerated ageing for a total of 1500 hours; the design of this set of experiments is shown in Fig. 6.4.

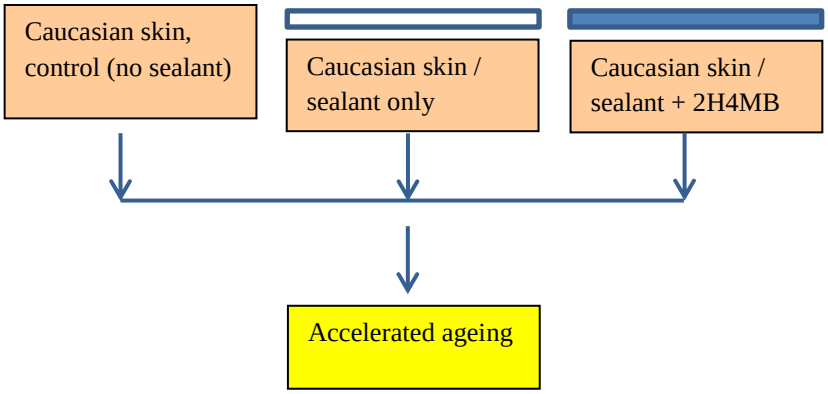


Fig. 6.4: Study design – Caucasian skin coloured samples without sealant (control), sealant only and sealant with UV-light absorber.

6.4. Methods

6.4.1. Fabrication of samples with intrinsic use of UV-light absorbers

For manufacture of silicone samples with incorporated UV-light absorbers, M511 base elastomer (Technovent) was coloured with the Alizarin Crimson pigment (Spectromatch); and the above materials were weighed as described in Chapter 3, section 3.2.1. Three different light absorbers included Semasorb, Uvinul and 2H4MB were individually added to the elastomer / colourant mix at 1% weight. The elastomer / colourant / UV-light absorber compound was then mixed, packed into the PTFE mould and processed as described in Chapter 3, section 3.2.1.

6.4.2. Fabrication of samples with Parylene coating and mixing of silicone in a nitrogen environment

6.4.2.1. Parylene coating

For fabrication of test specimens, M511 elastomer (Technovent) was coloured with Alizarin Crimson and Malachite Green pigments (Spectromatch). Base elastomer and pigments were weighed, mixed and processed as described in Chapter 3, section 3.2.1.; samples were subsequently sent to a specialised company, SCS, for Parylene coating. For investigations in this current study, Parylene HT was applied at a thickness of 12 to 13 microns. This Parylene variant has been used as it is recommended for applications in which long term UV-light stability is required.

6.4.2.2. Mixing of silicone in a nitrogen environment

An attempt was made to manufacture silicone samples that contained no trapped oxygen. The test samples for this part of investigations were manufactured at DSTL, Fort Halstead, Kent. M511 base elastomer (Technovent) and two different pigments, Alizarin Crimson and Malachite Green (Spectromatch), were used for

this part of experiments. Base elastomer and pigments were weighed as described in Chapter 3, section 3.2.1. M511 silicone and pigments were first pre-mixed by hand using a spatula and then placed into the Speedmixer at 1800 rpm for 30 secs to achieve homogeneity of the mix. The mixing pot, still with its lid in place, was then placed into a vacuum desiccator and the air evacuated.

The desiccator, Speedmixer, PTFE lined mould for fabrication of test samples, and spatulas were placed inside a large plastic glove bag inside a fume cupboard. The bag was then inflated using oxygen free nitrogen. The desiccator was opened and the pigmented elastomer received two further mixing cycles in the Speedmixer (1800 rpm, 30 secs) inside the glove bag. Within this enclosed nitrogen environment, the coloured silicone elastomer was then carefully loaded into the PTFE lined mould using a spatula and the mould closed hand tight using a wrench.

The closed mould was then removed from the plastic glove bag and placed into a dry heat oven and cured as described in Chapter 3, section 3.2.1. Following polymerisation, the test specimens were divested and immediately placed into plastic packaging that provided a physical barrier to the ingress of oxygen and with an oxygen absorbing sachet added. The packages were sealed and stored in darkness until environmental conditioning of test samples was commenced.

6.4.3. Fabrication of samples with extrinsic sealant

6.4.3.1. Sealant only

For manufacture of test specimens with a surface silicone sealant layer, a 0.8 mm thick polypropylene vacuum forming sheet was cut to fit exactly into each sample grid of the PTFE lined mould which was used for manufacture of colour stability test specimen, Chapter 3, section 3.2.1. The polypropylene sheet was utilised as a spacer to produce room for subsequent application of the silicone surface sealant. A polypropylene sheet of 0.8 mm thickness was chosen as it represents the

commonly applied thickness of silicone used to seal extrinsic tinting on the surface of maxillofacial prostheses.

For this set of experiments, non-pigmented M511 and elastomer coloured with Alizarin Crimson, Logwood Maroon, Indian Yellow and a combination of pigments to establish a Caucasian skin tone were manufactured. M511 elastomer (Technovent) and pigments (Spectromatch) were weighed and mixed as described in Chapter 3, section 3.2.1. Non-pigmented and pigmented elastomer was then packed into the PTFE lined mould, on the top of the polypropylene sheet, and subsequently processed as described in Chapter 3, section 3.2.1.

Following polymerisation, silicone specimens were divested with great care and the polypropylene sheet carefully peeled away from the surface of silicone samples. The samples were then placed back into the grids of the PTFE mould in order to apply the P799 silicone surface sealant (Technovent). P799 was used in accordance to the manufacturer instructions with a ratio of 1:1; equal amounts of Part A and Part B (7.5 g each) were weighed and mixed with a spatula to produce a homogeneous mix.

With silicone specimens in place inside the PTFE mould, P799 was applied on the surface of silicone samples using a spatula. This was undertaken with great care in order to avoid any air entrapments. Once the sealant was applied, the cover of the PTFE mould was placed on the top of the mould carrying the samples and applied surface sealant. The mould was then closed and its screws secured to hand tight using a wrench. The mould was then left on the bench for curing at room temperature for one hour. Following polymerisation, samples were carefully removed from the mould and stored in a light safe container until base colour measurements were performed and weathering of samples was commenced.

6.4.3.2. Surface sealant and UV-light absorber

Test specimens for this set of investigations were coloured, mixed and polymerised as described in the above section, 6.4.3.1. Before applying the surface sealant layer, 1% weight of 2H4MB was added to 15 grams of P799 sealant. The silicone / UV-light absorber compound was first carefully mixed with a spatula and subsequently mixed utilising the speedmixer DAC 150 FVZ-K (Hauschild Engineeering) in order to achieve homogeneity of the material mix. It was then placed on the surface of test specimens using a spatula and processed as described in the above section, 6.4.3.1.

6.4.4. Fabrication of Caucasian skin coloured samples

6.4.4.1. Fabrication of samples without sealant (control)

In this part of investigations, Caucasian skin coloured silicone samples were manufactured without surface sealant and served as a control. M511 silicone elastomer was coloured with a pigment mix resulting in a Caucasian skin tone as previously used in Chapter 3, section 3.2.1. Silicone and pigments were weighed, mixed and processed as also described in this section.

6.4.4.2. Fabrication of samples with sealant layer only

For manufacture of Caucasian skin coloured samples with P799 silicone surface sealant only; elastomer, pigments and silicone surface sealant were weighed, mixed and processed as described in section 6.4.3.1. of this chapter.

6.4.4.3. Fabrication of samples with sealant layer and UV-light absorber

Fabrication of Caucasian skin coloured test specimens with P799 silicone surface sealant and incorporated 2H4MB UV-light absorber was performed as explained in section 6.4.3.2. of this chapter.

6.4.5. Weathering of test samples

Test specimens in this part of the research project were exposed to two different environments including storage in darkness and / or accelerated ageing in a weathering chamber for either 1000 hours, 1500 hours or 3000 hours. Weathering was performed as previously described in Chapter 3, section 3.2.2.

6.4.6. Measurement of colour and calculation of colour differences

Colour measurement of all silicone elastomer test specimens and subsequent calculation of colour differences was undertaken as applied earlier in Chapter 3, section 3.2.3.

6.4.7. Statistical analysis

Statistical analysis of data was undertaken as described in Chapter 3.

6.5. Results

All colour measurement data and corresponding calculated $\overline{\Delta E}$ for experiments from this part of investigations is provided in Appendix M on the CD which is enclosed with this thesis.

6.5.1. Intrinsic use of UV-light absorbers

The $\overline{\Delta E}$ values following 1000 hours of accelerated ageing were lowest for Alizarin Crimson control with 1.67 (B) and highest for Alizarin Crimson Uvinul with 19.17 (W). From the three tested UV-light absorbers, lowest $\overline{\Delta E}$ values were calculated for Alizarin Crimson 2H4MB with 1.88 (B). The intrinsic use of UV-light absorbers for samples stored in darkness resulted in smaller colour changes than did accelerated ageing; lowest colour changes were observed for Alizarin Crimson Control with 0.78 $\overline{\Delta E}$ (B) and highest for Alizarin Crimson Semasorb with 1.66 $\overline{\Delta E}$ (W). A univariate summary of data is provided in Table 6.2.

Environment	Pigment	Black	White
		$\overline{\Delta E}$, sd	$\overline{\Delta E}$, sd
Accelerated ageing	Alizarin Crimson control	1.67, 0.34	1.87, 0.41
	Alizarin Crimson Semasorb	7.20, 1.97	7.41, 1.95
	Alizarin Crimson Uvinul	19.01, 1.37	19.17, 1.42
	Alizarin Crimson 2H4MB	1.88, 0.26	2.03, 0.27
Darkness	Alizarin Crimson control	0.78, 0.23	1.03, 0.19
	Alizarin Crimson Semasorb	1.36, 0.22	1.66, 0.20
	Alizarin Crimson Uvinul	1.30, 0.35	1.47, 0.34
	Alizarin Crimson 2H4MB	1.39, 0.32	1.58, 0.35

Table 6.2: Univariate summary statistics for $\overline{\Delta E}$ after 1000 hours exposure to accelerated ageing and darkness for all pigment and background combinations.

There was a significant effect of method (type of UV-light absorber), time and the interaction of method and time on the $\overline{\Delta E}$ of all test groups ($p = 0.001$) when exposed to accelerated ageing and darkness storage and measured over both, black and white backgrounds. Šídák's multiple comparisons of means test showed that for samples exposed to accelerated ageing, Alizarin Crimson control and Alizarin Crimson with 2H4MB were not statistically significantly different from each other. For test specimens stored in darkness, Alizarin Crimson control and Alizarin Crimson Uvinul were not statistically significantly different from each other, as well as Alizarin Crimson Uvinul from Alizarin Crimson Semasorb and Alizarin Crimosn 2H4MB; and a summary is provided in Table 6.3.

Test group	Šídák			
	Accelerated ageing		Darkness	
	Black	White	Black	White
Alizarin Crimson control	A	A	A	A
Alizarin Crimson Semasorb			B	B
Alizarin Crimson Uvinul			A B	A B
Alizarin Crimson 2H4MB	A	A	B	B

Table 6.3: Šídák's multiple comparison of pigment, environmnent and background.

Groups sharing the same letter are not statistically significantly different.

The calculated $\overline{\Delta E}$ were similar for samples measured over the black and white background. Slightly higher $\overline{\Delta E}$ were calculated for the white background and these $\overline{\Delta E}$ and associated 95% confidence intervals for samples of all test groups and UV-light absorber at each time period are illustrated in the corresponding figures (Figs. 6.5 and 6.6). $\overline{\Delta E}$ and associated 95% confidence intervals for samples of all test groups and UV-light absorber at each time period when assessed over the black background are provided in Appendix N (Figs. 5 and 6) and stored on the CD which is enclosed with this thesis.

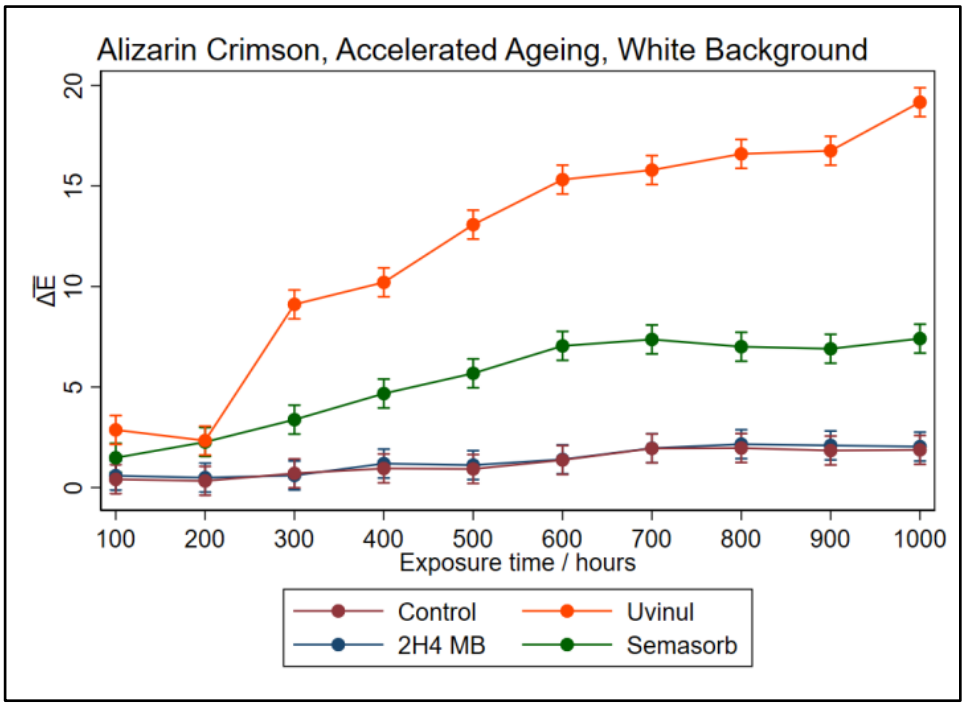


Fig. 6.5: $\overline{\Delta \mathbf{E}}$ values and associated 95 % confidence interval at each time period.

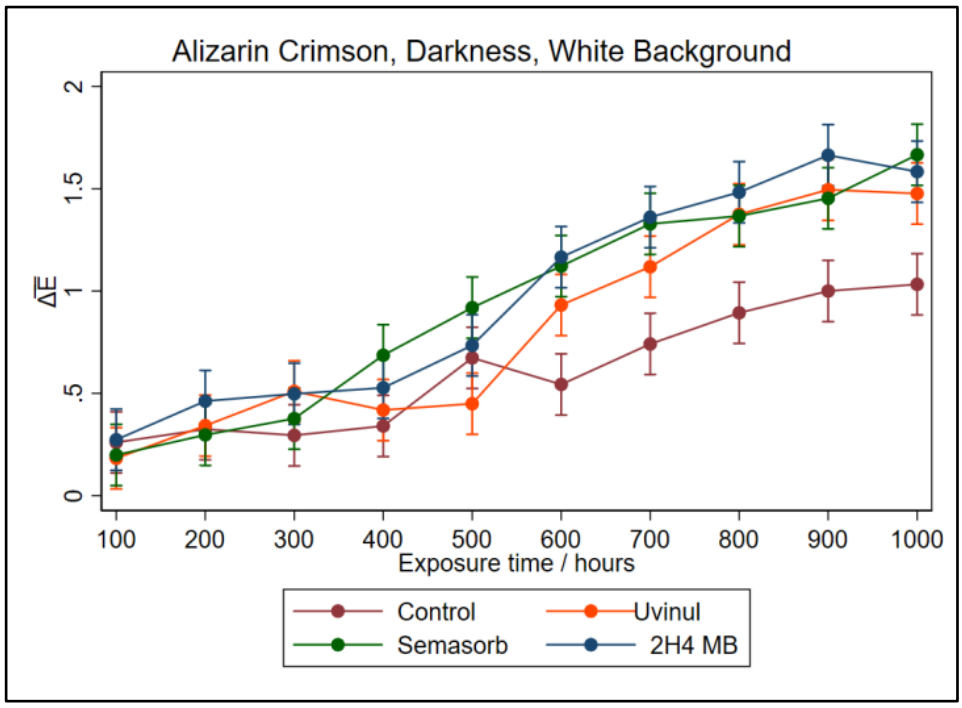


Fig. 6.6: $\overline{\Delta \mathbf{E}}$ values and associated 95 % confidence interval at each time period.

6.5.2. Parylene coating and mixing of silicone in a nitrogen environment

For samples exposed to accelerated ageing, Malachite Green control samples demonstrated lowest $\overline{\Delta E}$ values of 1.33 (B) and highest values were observed for Alizarin Crimson control with 2.67 (W). For darkness samples, lowest $\overline{\Delta E}$ values were calculated for Malachite Green control with 0.50 (W) and highest for Malachite Green Parylene with 1.72 (B). Comparing Alizarin Crimson and Malachite Green when exposed to accelerated ageing and darkness storage showed that both methods, silicone mixing under nitrogen and Parylene coating, reduced the $\overline{\Delta E}$ values for Alizarin Crimson coloured test specimens but increased for Malachite Green. A univariate summary of data is shown in Table 6.4.

Environment	Pigment	Black	White
		$\overline{\Delta E}$, sd	$\overline{\Delta E}$, sd
Accelerated Ageing	Alizarin Crimson control	2.41,0.32	2.67, 0.36
	Alizarin Crimson Parylene	1.85, 0.33	1.83, 0.34
	Alizarin Crimson nitrogen	2.33, 0.23	2.55, 0.19
	Malachite Green control	1.33, 0.29	1.71, 0.34
	Malachite Green Parylene	2.63, 0.21	2.59, 0.24
	Malachite Green nitrogen	1.46, 0.42	1.68, 0.43
Darkness	Alizarin Crimson control	1.00, 0.24	1.24, 0.21
	Alizarin Crimson Parylene	0.75, 0.43	0.76, 0.43
	Alizarin Crimson nitrogen	0.87, 0.42	1.02, 0.47
	Malachite Green control	0.56, 0.18	0.50, 0.15
	Malachite Green Parylene	1.72, 0.36	1.70, 0.37
	Malachite Green nitrogen	1.02, 0.49	1.00, 0.55

Table 6.4: Univariate summary statistics for $\overline{\Delta n}$ after 1500 hours exposure to accelerated ageing and darkness for all pigment and background combinations.

For Alizarin Crimson control, Aliarin Crimson Parylene and Alizarin Crimson nitrogen samples stored in darkness; elastomer treatment (Parylene coating and mixing in nitrogen environment) had no statistically significant effect whereas time and interaction of elastomer treatment and time were statistically significant ($p = 0.001$) when measured over both backgrounds. For all Alizarin Crimson test groups exposed to accelerated ageing and all Malachite Green test groups stored in darkness and exposed to accelerated ageing, there was a statistically significant effect of time, elastomer treatment (method) and the interaction of time and method when assessed over both backgrounds ($p = 0.001$).

Šídák's multiple comparisons of means test showed that for samples exposed to accelerated ageing, Alizarin Crimson and Malachite Green control samples and Alizarin Crimson and Malachite Green nitrogen were not statistically significantly different from each other. It was different for darkness samples, where for Alizarin Crimson, all test groups were not statistically significantly different from each other when measured over black and white; whereas for Malachite Green, all test groups were statistically significantly different from each other when measured over black. Malachite Green Control and Malachite Green nitrogen were not different from each other when measured over the white background (Table 6.5).

Test group	Accelerated ageing		Darkness	
	Black	White	Black	White
	Šídák	Šídák	Šídák	Šídák
Alizarin Crimson control	A	A	A	A
Alizarin Crimson nitrogen	A	A	A	A
Alizarin Crimson Parylene			A	A
Malachite Green control	A	A		A
Malachite Green nitrogen	A	A		A
Malachite Green Parylene				

Table 6.5: Šídák's multiple comparison of pigment, environmnent and background.

Groups sharing the same letter are not statistically significantly different.

The calculated $\overline{\Delta E}$ were similar for samples measured over the black and white background. Slightly higher $\overline{\Delta E}$ were calculated for the white background and these $\overline{\Delta E}$ and associated 95% confidence intervals for samples of all test groups and elastomer treatment at each time period are illustrated in the corresponding figures (Figs. 6.7 to 6.10). $\overline{\Delta E}$ and associated 95% confidence intervals for samples of all test groups and elastomer treatment at each time period when assessed over the black background are shown in Appendix O (Figs. 7 to 10).

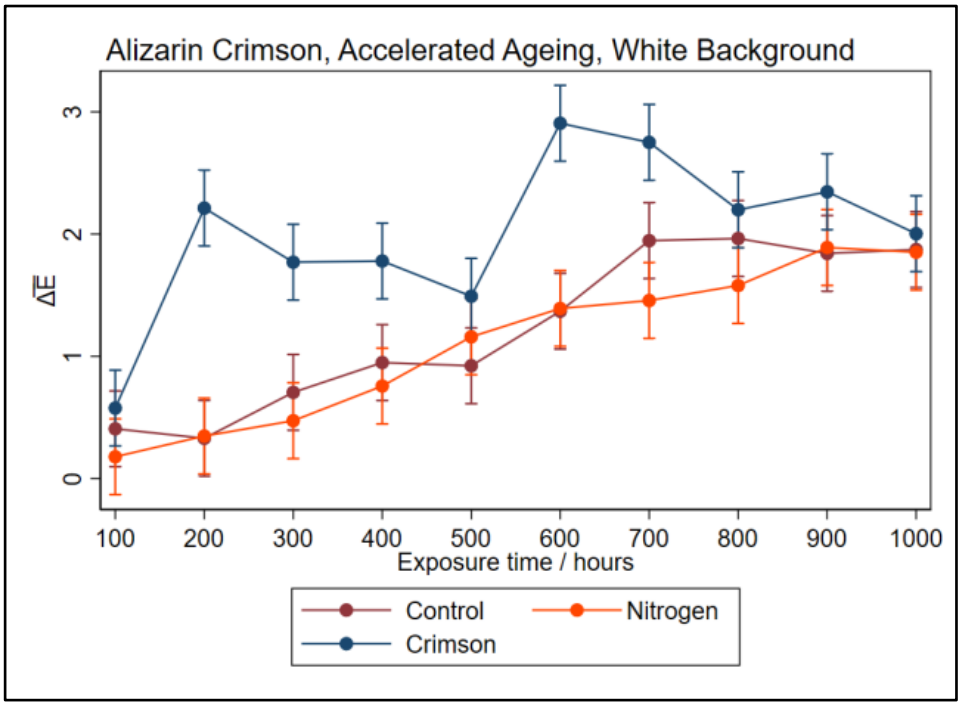


Fig. 6.7: $\overline{\mathbf{\Delta E}}$ values and associated 95% confidence interval at each time period.

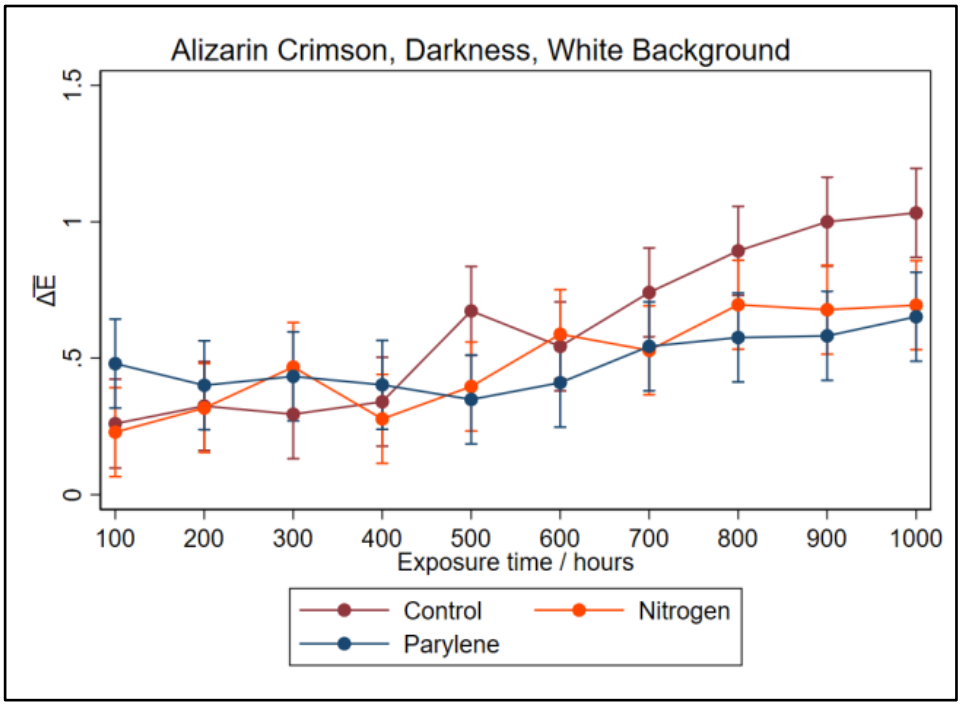


Fig. 6.8: $\overline{\mathbf{\Delta E}}$ values and associated 95% confidence interval at each time period.

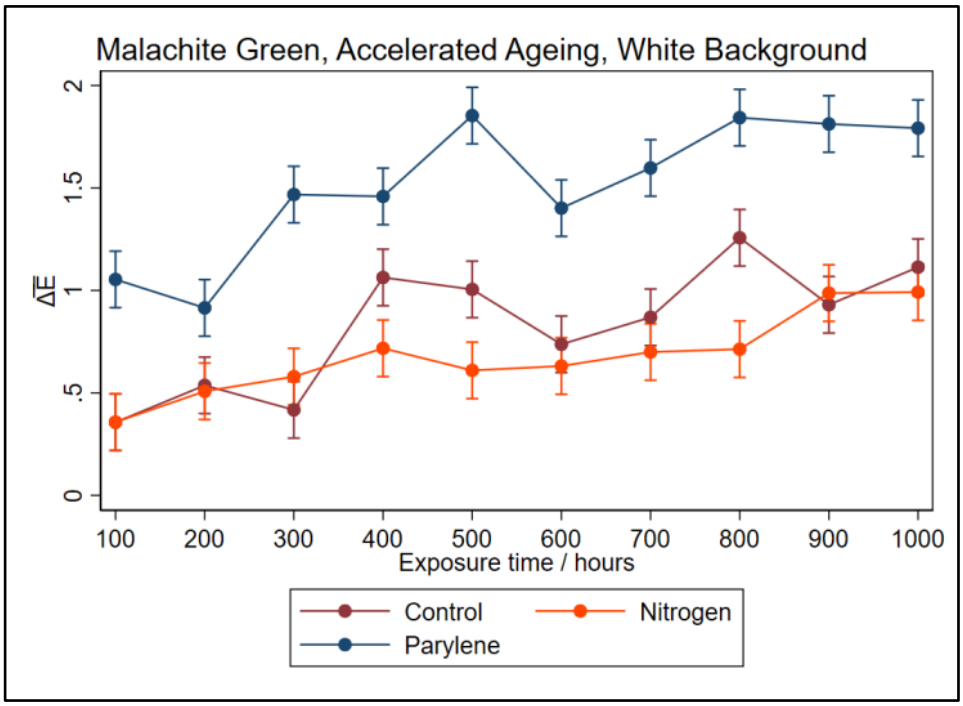


Fig. 6.9: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

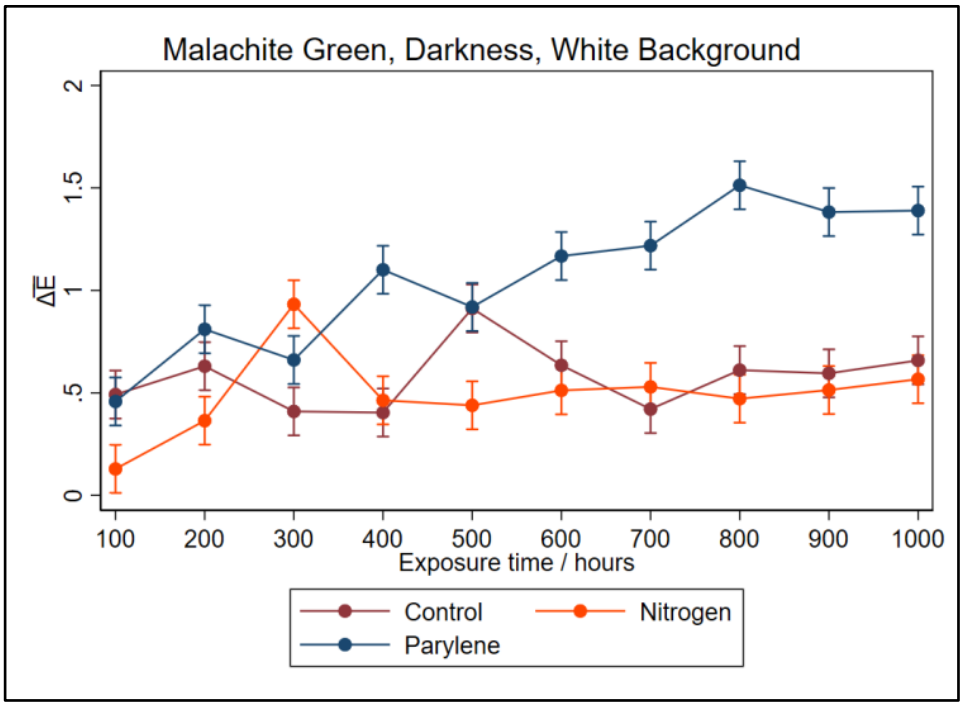


Fig. 6.10: $\overline{\mathbf{\Delta E}}$ values and associated 95% confidence interval at each time period.

6.5.3. P799 surface sealant; sealant only and sealant / UV-light absorber

Comparison of specimens with the P799 extrinsic sealant layer only and P799 extrinsic sealant / 2H4MB UV-light absorber showed lower $\overline{\Delta E}$ for specimens with P799 / 2H4MB apart from two colourants, Logwood Maroon and Indian Yellow, where the $\overline{\Delta E}$ was higher. The $\overline{\Delta E}$ for test specimens with P799 only ranged from 0.38 (Logwood Maroon) to 3.09 $\overline{\Delta E}$ (Indian Yellow); for test specimens with P799 / 2H4MB from 0.41 (Logwood Maroon) to 3.52 $\overline{\Delta E}$ (Indian Yellow). Generally, Logwood Maroon coloured test specimens demonstrated lowest and Indian Yellow highest colour changes. A univariate summary of data is provided in Table 6.6. For some individually coloured test specimens with sealant and UV-light absorber $\overline{\Delta E}$ increased when compared with the sealant only samples; $\overline{\Delta E}$ decreased for a mix of pigments in the Caucasian skin tone from 2.51 $\overline{\Delta E}$ (sealant only) to 1.56 $\overline{\Delta E}$ (sealant / UV-light absorber).

Test groups	Background	Sealant	Sealant / UV
		Mean, sd	Mean, sd
Non-pigmented	W	2.23, 0.11	1.44, 0.12
	B	1.30, 0.07	0.94, 0.07
Logwood Maroon	W	0.38, 0.09	0.41, 0.10
	B	0.38, 0.10	0.41, 0.15
Alizarin Crimson	W	0.49, 0.07	0.45, 0.07
	B	0.44, 0.08	0.42, 0.08
Indian Yellow	W	3.09, 0.08	3.52, 0.11
	B	2.74, 0.10	3.10, 0.08
Caucasian skin	W	2.50, 0.19	1.57, 0.04
	B	2.51, 0.19	1.56, 0.03

Table 6.6: Univariate summary statistics for $\overline{\Delta E}$ for all pigment and background combinations with a sealant layer or sealant / UV.

LMM analysis of data showed statistically significant effect of time, sealing method, and the interaction of time, sealing method on the $\overline{\Delta E}$ of all test groups ($p = 0.001$) apart from Logwood Maroon and Alizarin Crimson, where the sealing method had no statistically significant effect for both, black and white backgrounds (Table 6.7). A pairwise comparison showed that there was no statistically significant difference between Logwood Maroon and Alizarin Crimson, sealant only and sealant / UV-light absorber (Table 6.8).

Test group	Background	p		
		Time	Sealant method	Time # sealant method
Non-pigmented	W	0.001	0.001	0.001
	B	0.001	0.001	0.001
Logwood Maroon	W	0.001	0.762	0.001
	B	0.001	0.800	0.001
Alizarin Crimson	W	0.001	0.174	0.001
	B	0.001	0.400	0.001
Indian Yellow	W	0.001	0.001	0.001
	B	0.001	0.001	0.001
Caucasian skin	W	0.001	0.001	0.001
	B	0.001	0.001	0.001

Table 6.7: Summary of LMM analysis showing main effects for pigment, background, time and method, and the time#method interaction.

Test group	Black	White
Non-pigmented sealant		
Non-pigmented sealant / UV		
Logwood Maroon sealant	A	A
Logwood Maroon sealant / UV	A	A
Alizarin Crimson sealant	A	A
Alizarin Crimson sealant / UV	A	A
Indian Yellow sealant		
Indian Yellow sealant / UV		
Caucasian skin sealant		
Caucasian skin sealant / UV		

Table 6.8: Šídák's multiple comparison of the pigments by backgound. Groups sharing the same letter are not statistically significantly different.

The colour of all test specimens was assessed every 100 hours and the calculated $\overline{\Delta E}$ and associated 95% confidence intervals for non-pigmented specimens and Caucasian skin coloured samples for both backgrounds and methods at each time period are illustrated in Figs. 6.11 to 6.14. $\overline{\Delta E}$ and associated 95% confidence intervals for all remaining test groups are shown in Appendix P (Figs. 11 to 16).

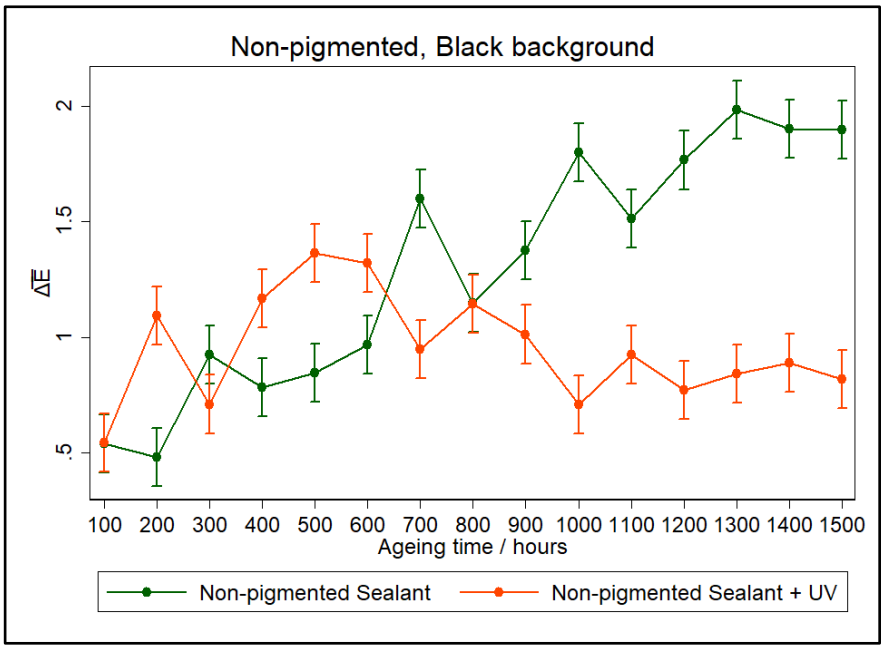


Fig. 6.11: $\overline{\Delta E}$ and associated confidence intervals for non-pigmented specimens with sealant and sealant / UV-light absorber following1500 hours of accelerated ageing.

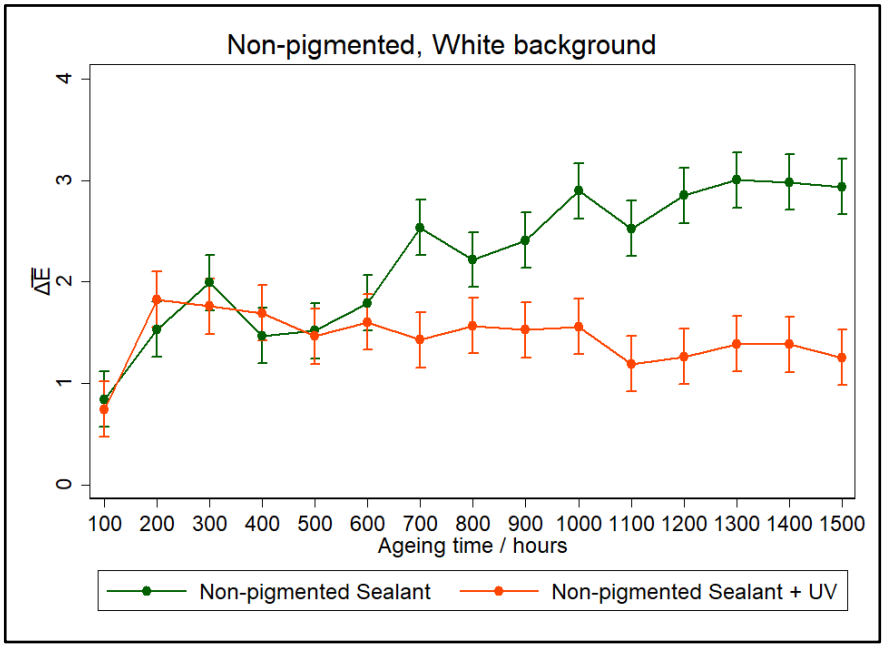


Fig. 6.12: $\overline{\mathbf{\Delta E}}$ and associated confidence intervals for non-pigmented specimens with sealant and sealant / UV-light absorber following 1500 hours of accelerated ageing.

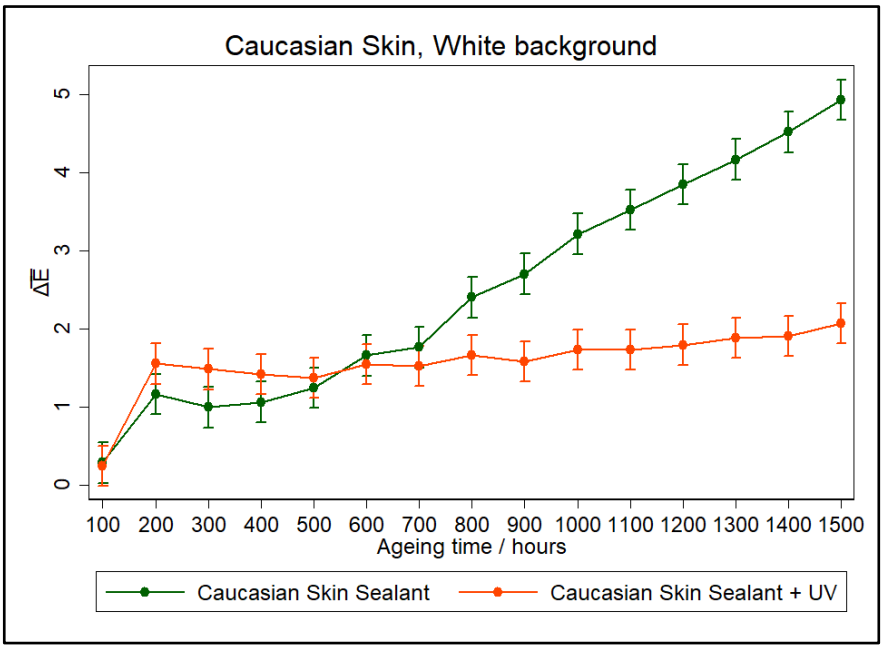


Fig. 6.13: $\overline{\mathbf{\Delta E}}$ and associated confidence intervals for Caucasian skin with sealant and sealant / UV-light absorber following 1500 hours of accelerated ageing.

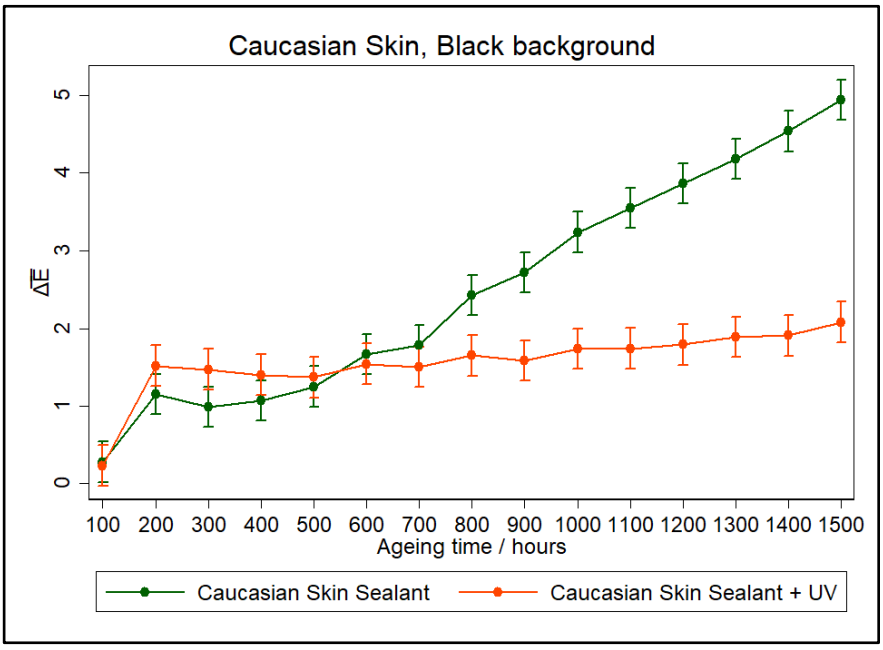


Fig. 6.14: $\overline{\mathbf{\Delta E}}$ and associated confidence intervals for Caucasian skin with sealant and sealant / UV-light absorber following 1500 hours of accelerated ageing.

6.5.4. Caucasian skin coloured samples

6.5.4.1. Surface sealant and UV-light absorber at 1% and 2% weight

Comparison of Caucasian skin coloured control samples (non-treated) with Caucasian skin coloured samples with sealant only and samples with sealant / 2H4MB UV-light absorber at 1% and 2% after 1500 hours of accelerated ageing showed largest colour changes for control samples with $\overline{\Delta E}$ of 3.25 (B) and 3.26 (W). With application of the surface sealant only, lower colour changes of 1.99 (B) and 2.00 (W) were observed when comparing them with non-treated control samples. However, lowest colour changes of 1.18 (B) and 1.21 (W) were calculated for Caucasian skin with surface sealant / 1% UV-light absorber. A univariate of summary data is provided in Table 6.9.

Test group	Black	White
	$\overline{\Delta E}$, sd	$\overline{\Delta E}$, sd
Caucasian skin control	3.25, 0.71	3.26, 0.71
Caucasian skin with P799	1.99, 0.21	2.00, 0.21
Caucasian skin with P799 / 1% 2H4MB	1.18, 0.07	1.21, 0.07
Caucasian skin with P799 / 2% 2H4MB	1.21, 0.09	1.23, 0.09

Table 6.9: Univariate summary statistics for $\overline{\Delta E}$ for all test group and background combinations.

LMM analysis of data showed there was a statistically significant effect of sealing method, time and interaction of method and time on the $\overline{\Delta E}$ ($p = 0.001$) when samples were measured over both backgrounds. Šídák's multiple comparisons of means test was applied and showed that Caucasian skin coloured samples with sealant / 1% and 2% were not statistically significantly different from each other. The calculated $\overline{\Delta E}$ and associated 95% confidence intervals for all sealant methods and both backgrounds at each time period are illustrated in Figs. 6.15 and 6.16.

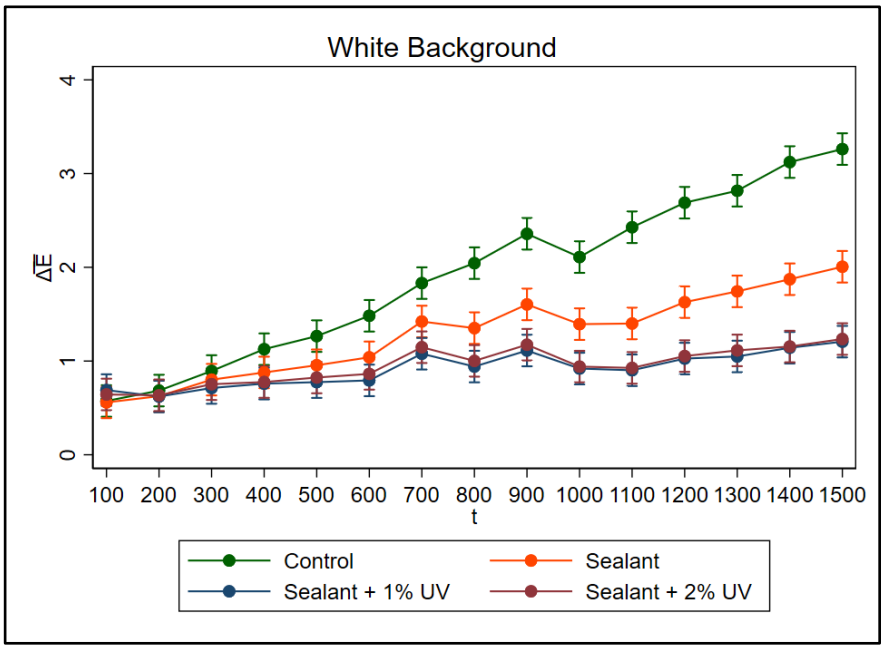


Fig. 6.15: $\overline{\Delta E}$ and associated confidence intervals for test groups of Caucasian skin coloured specimens following 1500 hours of accelerated ageing.

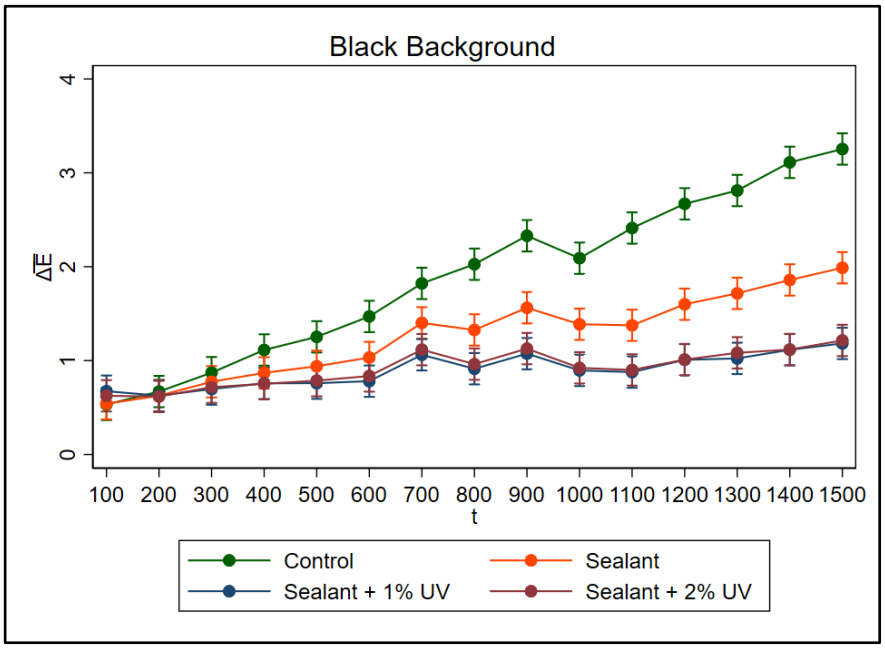


Fig. 6.16: $\overline{\Delta \mathbf{E}}$ and associated confidence intervals for test groups of Caucasian skin coloured specimens following 1500 hours of accelerated ageing.

6.5.4.2. Surface sealant and UV-light absorber at 1% weight versus control

A summary of $\overline{\Delta E}$ for Caucasian skin control and Caucasian skin with sealant / 1% UV-light absorber is shown in Table 6.10. Caucasian skin control samples and Caucasian skin with sealant / 1% UV-light absorber were exposed to a prolonged period of 3000 hours of accelerated ageing. When measured over both backgrounds, there was a statistically significant effect of sealing method, time and interaction of method and time on the $\overline{\Delta E}$ ($p = 0.001$). Šídák's multiple comparisons of means test was applied and showed that all test groups were statistically significantly different from each other.

Test group	Black	White
	3000 h	3000 h
	$\overline{\Delta E}$, sd	$\overline{\Delta E}$, sd
Caucasian skin control	5.38, 0.58	5.41, 0.58
Caucasian skin sealant / 1% UV-light absorber	2.03, 0.19	2.06, 0.58

Table 6.10: Univariate summary statistics for $\overline{\Delta E}$ after 3000 hours exposure to accelerated ageing for all pigment and background combinations.

$\overline{\Delta E}$ and associated 95% confidence intervals for both test groups, backgrounds at each time period are illustrated in Figs. 6.17 and 6.18.

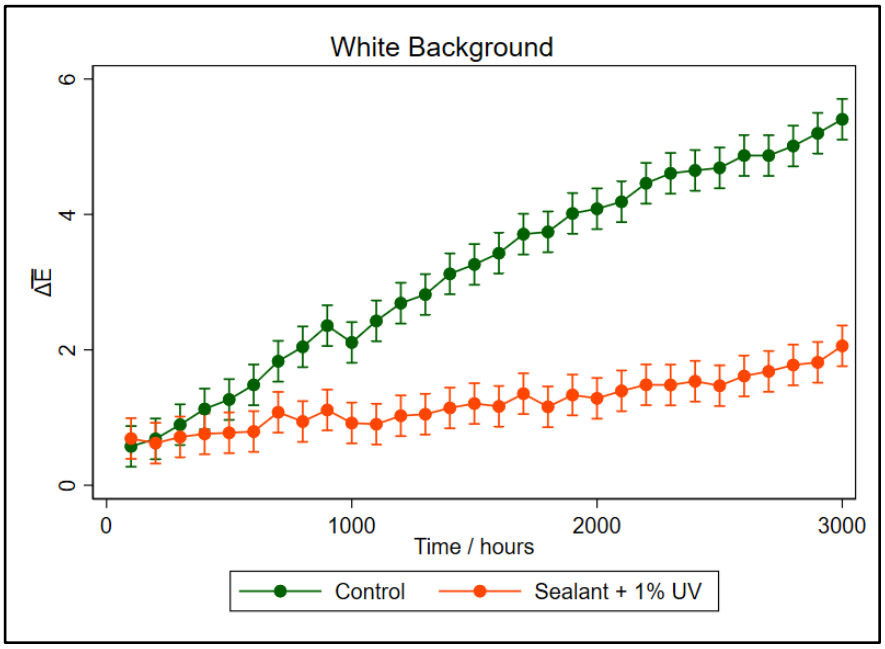


Fig. 6.17: $\overline{\mathbf{\Delta E}}$ and associated confidence intervals for test groups of Caucasian skin coloured specimens following 3000 hours of accelerated ageing.

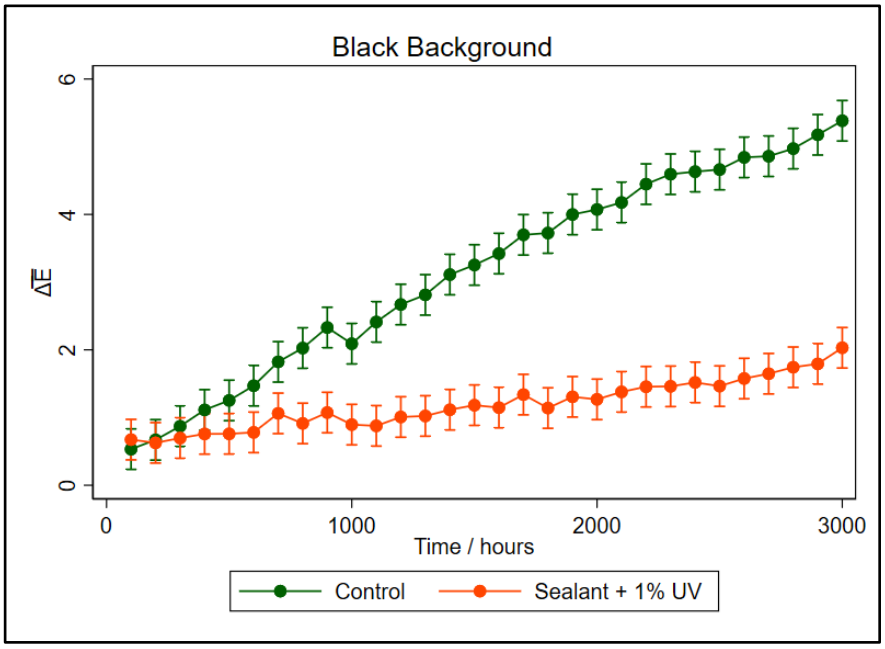


Fig. 6.18: $\overline{\mathbf{\Delta E}}$ and associated confidence intervals for test groups of Caucasian skin coloured specimens following 3000 hours of accelerated ageing.

6.6. Discussion

This part of the study was designed to investigate the effect of using two different silicone surface sealant techniques involving Parylene coating and the application of a commercially available silicone extrinsic sealant as well as the use of UV-light absorbers in order to improve the colour stability of maxillofacial elastomer. The results showed improved colour stability for some pigments, the combination of pigments, and for the use of a silicone surface sealant in combination with 2H4MB UV-light absorber. Therefore, we reject the null hypothesis for this part of investigations.

6.6.1. Intrinsic use of UV-light absorbers

6.6.1.1. Accelerated ageing

Colour changes of maxillofacial prostheses have been frequently observed in clinical practice. They have been related to external environmental factors including UV-light, humidity, air pollution, colour instability of pigments and elastomer as well as influences caused by patients such as prolonged direct contact of silicone elastomer with skin, prostheses handling and cleaning measures and smoking. However, UV-light has been determined as one main reason for colour changes of facial appliances in clinical service (Gary *et al.* 2001; Hatamleh and Watts 2010[a]; Koran *et al*. 1979; Lemon *et al*. 1995).

In this current research, 1% by weight of three different light absorbers (Semasorb, Uvinul, 2H4MB) were tested and was in agreement with Kheur *et al.* (2016) who also used 1% of UV-light absorber, UVA (Chimassorb 81; BASF) and 1% of hindered amine light stabiliser, HALS (Uvinul 5050; BASF). However, Lemon *et al*. (1995) used 0.1 and 0.25% by weight of Spectra-sorb UV-5411 (American Cyanamid Co.) and Tran *et al*. (2004) applied a 1:1 ratio of UVA and HALS (Tinuvin 213 and Tinuvin 123, respectively; both Ciba Specialty Chemicals) at a concentration of 0.75% by weight. Whereas Bryant *et al.* (1994) used 5% weight of a UV-light absorber (PABA; Aldrich Chemical Company Inc.)

and Han *et al*. (2013) investigated the effect of a UV mineral-based light protecting agent (LP; Colore Science) at 5, 10 and 15% weight. Various UV-light absorbers and light stabilisers at different percentages have been used in the reviewed studies and this makes it difficult to compare them with each other and with the current research.

In this current study, Semasorb, Uvinul and 2H4MB were directly mixed into M511 base elastomer which was coloured with Alizarin Crimson; and test samples were exposed to 1000 hours of accelerated ageing in a weathering chamber. The results showed a significant effect of UV-light absorber, time and the interaction of UV-light absorber and time on the $\overline{\Delta E}$ of all test groups ($p = 0.001$) when exposed to accelerated ageing and darkness storage and when measured over black and white backgrounds. When exposed to accelerated ageing, highest colour changes were observed for Uvinul with $\overline{\Delta E}$ values of 19.7 (W). Lowest colour changes for the intrinsic use of a UV-light absorber were obtained for 2H4MB with 1.88 (B) $\overline{\Delta E}$. However, non-treated Alizarin Crimson control samples demonstrated lowest $\overline{\Delta E}$ values of all test samples with 1.67 (B).

It was shown that two of the light absorbers, Uvinul and Semasorb, resulted in significant increase of colour changes of Alizarin Crimson coloured M511 elastomer; and it has been suggested that chemical interactions are likely to be the reason for the observed drastic changes in colour. However, no chemical analysis was performed to provide details on possible chemical reactions or material interactions. Furthermore, the use of Semasorb resulted in 'yellowing' of the surface of test specimens; light yellow coloured Semasorb particles may have migrated towards the surface of test specimens during the course of accelerated ageing (Fig. 6.19). All three light absorbers are from the same chemical group of benzophenones and used as UV-light absorbers in different fields such as cosmetics, sunscreens or UV protection of clothing. The use of 2H4MB with M511 elastomer still resulted in higher colour changes when compared with Alizarin Crimson control samples ($\overline{\Delta E}$ of 1.88 and 1.67, respectively) but showed promising results.

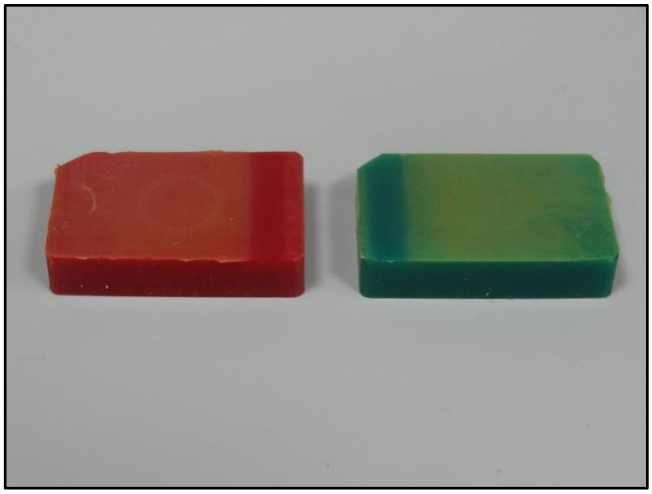


Fig. 6.19: Surface 'yellowing' of test samples with intrinsic Semasorb UV-light absorber.
(The vertical darker coloured stripe on the surface of test specimens represents an area where the surface of specimens was covered with the sample holder and was protected from direct UV-light exposure.)

Bryant *et al.* (1994) mixed 5% by weight of para-amino benzoic acid (PABA; Aldrich Chemical Company Inc) into MDX-4-4210 and exposed treated and non-treated control samples to UV-light for 300 hours. The results showed that application of the photo protective agent resulted in drastic colour changes of 17.76 $\overline{\Delta E}$ in comparison to 2.26 $\overline{\Delta E}$ for control specimens. This was in agreement with observations in this current study for Uvinul which resulted in $\overline{\Delta E}$ values of 19.7 (W).

Lemon *et al*. (1995) incorporated 0.1 and 0.25% by weight of Spectra-sorb UV-5411 (American Cyanamid Co.) into a mix of MDX4-4210 and type A medical adhesive (Dow Corning) which was coloured with oil-based pigments and kaolin (Factor II). Test samples were exposed to accelerated ageing and outdoor weathering in Florida, each to a total of 450 kJ m^{-2} radiant energy. The authors reported 1.39 $\overline{\Delta E}$ for control samples and 1.91 and 2.01 $\overline{\Delta E}$ for samples with incorporated 0.1% and 0.25% light absorber, respectively. However, lower colour changes were obtained for samples exposed to outdoor weathering. Lemon *et al.*

concluded that UV-5411 did not protect test specimens from colour changes. These observations were similar to the colour changes observed for 2H4MB in this current study, where the use of light absorber resulted in slightly higher colour changes when compared with control samples.

Han *et al*. (2013) used a UV mineral-based protecting agent (LP; Colore Science), which is a commercial cosmetic UV-light blocking powder, as an opacifier as well as dry pigments and functional intrinsic pigments (Factor II) to colour a mix of MDX4-4210 and medical adhesive Type A elastomer (Factor II). Test specimens were exposed to accelerated ageing in a weathering chamber (total of 450 kJ m^{-2}) and the results showed that for non-pigmented specimens, the use of UV-light absorber and addition of 15% of silicone white pigment produced small colour changes of 0.8 $\overline{\Delta E}$. However, a mix of pigments with added 5% or 15% of UV-light absorber resulted in even slightly lower colour changes of 0.7 $\overline{\Delta E}$. Smallest colour changes for pigments were obtained for red with 15% and yellow with 10% of UV-light absorber. These results are lower than the colour changes observed for Alizarin Crimson with 2H4MB UV-light absorber in this current study with 1.88 $\overline{\Delta E}$ (B) and may be related to the much higher percent weight of UV-light absorber used by Han *et al.* as well as different elastomer and pigments used.

In a recently published paper by Kheur *et al.* (2016), the colour stability of Z004 silicone elastomer (Technovent) was investigated by adding a UV-light absorber (Chimassorb 81) and UV light stabiliser (Uvinul 5050; BASF) at a total concentration of 1% by weight. Test specimens were exposed to artificial ageing in a weathering chamber for 300 hours. The results showed that the UV-light absorber, Chimassorb 81, consistently showed least colour changes when compared with all other test groups and $\overline{\Delta E}$ values ranged from 0.51 to 1.11; highest colour changes were observed for control samples with a $\overline{\Delta E}$ of 1.48.

Although Kheur *et al*. (2016) used the same concentration of UV-light absorber as it was used in this current study, a direct comparison with the results obtained by Kheur *et al*. is impossible. Different elastomer and UV-light absorbers were

applied and accelerated ageing was only performed for 300 hours in the study by Kheur *et al.* At 300 hours of accelerated ageing of Alizarin Crimson coloured M511 elastomer with added 2H4MB light absorber in this current study, $\overline{\Delta E}$ values of 0.60 (W) and 0.57 (B) were obtained and $\overline{\Delta E}$ values of test samples ranged from 0.38 to 0.86 and were smaller than the colour changes observed by Kheur *et al*.

6.6.1.2. Storage in darkness

Different results were obtained for of Alizarin Crimson coloured elastomer with added UV-light absorbers stored in darkness. Lowest colour changes of test specimens were observed for Alizarin Crimson control with 0.78 $\overline{\Delta E}$ (B); and highest $\overline{\Delta E}$ values with intrinsic use of UV-light absorbers were calculated for Alizarin Crimson Semasorb light absorber with 1.66 (W). However, these smaller colour changes were expected as the influence of UV-light was excluded when storing test specimens in darkness and was in agreement with Bryant *et al.* (1994).

The storage of Alizarin Crimson coloured samples with incorporated Uvinul light absorber in darkness for 1000 hours caused ‘blooming’ and resulted in deposition of white particles on the surface of test samples (Fig. 6.20). It has been suggested that the liquid light absorber may have caused some chemical interactions with the elastomer and pigment. However, chemical analysis was not performed to substantiate this statement.

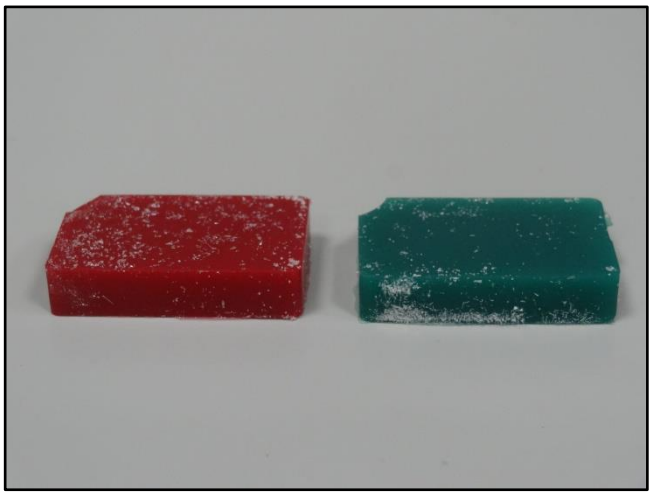


Fig. 6.20: ‘Blooming’ of test samples with intrinsic use of Uvinul UV-light absorber.

Summarising, even though still producing slightly higher colour changes of test specimens when compared with control samples, the 2H4MB UV-light absorber demonstrated promising results in combination with M511 elastomer and Alizarin Crimson pigment and was therefore used to carry out further investigations on the application of light absorbers.

6.6.2. Parylene coating and mixing silicone in nitrogen environment: A pilot study

A pilot study involved the application of Parylene coating on the surface of silicone elastomer samples. Alizarin Crimson and Malachite Green coloured test specimens were sent to a specialised company for application of the coating and it was aimed to determine as to whether Parylene coating of elastomer would provide a protective and ‘shielding’ layer on the surface of coloured M511 elastomer in order to increase the colour stability of maxillofacial elastomer and thereby reduce its colour changes.

Whilst there was no literature found on Parylene coating for specific facial prosthetic applications, numerous investigations have been identified on other medical applications (Chou *et al.* 2013; Hogg *et al.* 2014; Kuppusami and Oskouei 2015; Santos *et al.* 2013; Zhou *et al.* 2010). Zhou *et al.*, to highlight one example, investigated as to whether Parylene coating on denture bases and silicone elastomer can effectively reduce adhesion of Candida albicans and thus decrease the incidence of denture stomatitis. Specimen discs made from heat-cured PMMA (Lucitone 199; Dentsply International, York, PA) and A-2186 silicone (Factor II) were coated with Parylene N at a 5 nm thickness through chemical vapour deposition, using a commercial deposition system (Huaxing Nanotechnologies Co., Ltd., Guangdong, China). Candida albicans cells were subsequently seeded onto the PMMA and silicone discs, with and without Parylene coating; and the authors stated that on both, PMMA and silicone discs, Candida adherence and aggregation on the surface of specimens was significantly lower following Parylene surface coating.

The second experiment of this part of the study involved mixing of silicone base elastomer in an inert nitrogen environment with the aim to manufacture silicone samples that contained no trapped oxygen.

Samples for both applications, including Parylene coating and mixing of silicone in a nitrogen environment, were exposed to accelerated ageing and stored in darkness.

6.6.2.1. Accelerated ageing

No literature was found using Parylene coating and silicone mixing for colour stability testing of maxillofacial elastomers. There was a statistically significant effect of time, elastomer treatment (method) and the interaction of time and method when assessed over both backgrounds ($p = 0.001$) for all Alizarin Crimson and Malachite Green test groups when exposed to accelerated ageing. For both tested pigments, Parylene coating and mixing under nitrogen reduced the colour changes of specimens when compared with control samples. Parylene

coating of Alizarin Crimson coloured samples resulted in $\overline{\Delta E}$ values below the AT of 2 ΔE when compared with control samples, whereas the same coating method increased the colour changes of Malachite Green pigmented elastomer to above the AT in comparison to control samples.

Mixing of silicone in a nitrogen environment resulted in smaller colour changes and improved the colour stability for Alizarin Crimson but worsened the colour stability of Malachite Green pigmented test specimens.

6.6.2.2. Storage in darkness

For all Alizarin Crimson test groups, elastomer treatment (method) had no statistically significant effect; however, for all Malachite Green test groups there was a statistically significant effect of time, method and the interaction of time and method when assessed over both backgrounds ($p = 0.001$). From all test groups, lowest $\overline{\Delta E}$ values were calculated for Malachite Green control with 0.50 (W) and highest for Malachite Green Parylene with 1.72 (B). The colour stability of Malachite Green was adversely affected by Parylene coating but as no chemical analysis was performed, it can only be suggested that some material incompatibility was the reason for the increased colour changes.

Overall, Parylene coating reduced the $\overline{\Delta E}$ values for Alizarin Crimson coloured test specimens but increased them for Malachite Green. Some improvement as well as worsening of colour stability of pigmented maxillofacial elastomer was observed when applying Parylene coating or mixing the base elastomer in a nitrogen environment. Whereas more beneficial effects in terms of colour stability were obtained for Parylene, this coating method produced a surface hardening of the elastomer.

Although hardness testing was not performed for this particular application, a harder surface was noticeable by just touching the Parylene coated samples in comparison to control samples. Indenting of Parylene coated samples was difficult and resulted in surface creases of the coating and is shown in Fig. 6.21.

Furthermore, this coating technique was very costly. All of the above observations need to be considered when planning further research of Parylene coating for maxillofacial applications.

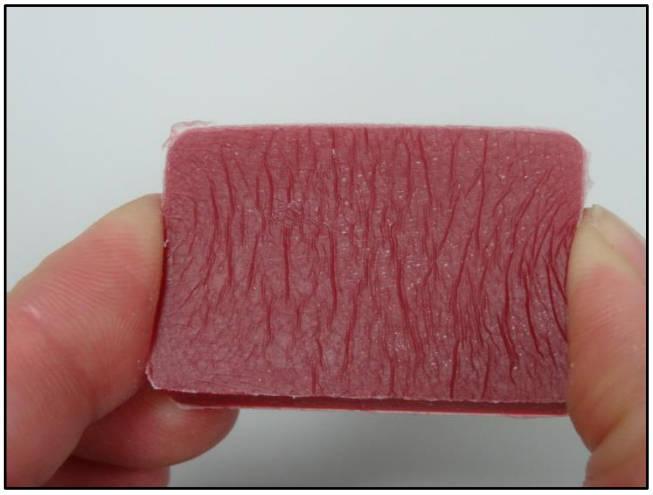


Fig. 6.21: Surface creasing of Parylene coated test sample.

Whereas mixing in a nitrogen environment showed some improvement in terms of colour stability for Alizarin Crimson, this technique also required a specific laboratory set-up and is not easily accomplished in the traditional maxillofacial laboratory. Therefore, further investigations need to be carefully considered as to whether the small observed colour stability improvements justify installation of specific devices and laboratory set-up which would be involved with this application.

6.6.3. Use of UV-light absorber in a surface sealant: A pilot study

6.6.3.1. 2H4MB in combination with surface sealant

The UV-light absorber demonstrating lowest colour changes of elastomer from the first part of experiments, 2H4MB, was used in combination with a commercial extrinsic silicone sealant, P799 (Technovent). This set of experiments represented a novel study as there is no literature on this application in maxillofacial prosthetic rehabilitation. The study design of these investigations

was based on observations made by Beatty *et al*. (1999) on the use of concentrated pigments in a thin surface layer in order to protect the underlying base elastomer and thereby reducing the overall colour changes of silicone.

Beatty *et al*. (1999) investigated the colour stability following accelerated ageing of a non-pigmented elastomer mix, consisting of 30% of A-2186 (Factor II) combined with 70% of 891 Type A adhesive (Dow Corning), and a thin applied pigment surface layer which represented a silicone sealing technique as it is applied when sealing extrinsic colouring on the surface of a maxillofacial prosthesis. This thin surface layer contained a 10-fold higher pigment concentration as it was used to intrinsically colour the base elastomer.
The authors reported significantly less colour changes to occur than did the thicker intrinsically coloured silicone samples with a lower pigment concentration. Beatty *et al*. concluded that the obtained observations supported the use of extrinsic colouring as a protective 'shielding' layer against adverse UV-light related colour changes, providing adequate pigment concentration in the surface sealant layer is used and this layer remains adherent.

In a pilot study, 2H4MB was added at 1% weight to a commercial surface sealant, P799 (Technovent), which was with 0.8 mm thickness applied on the surface of non-pigmented and pigmented Alizarin Crimson, Logwood Maroon, Indian Yellow and Caucasian skin coloured M511 elastomer test samples. Test specimens were exposed to accelerated ageing for 1500 hours. The results of these investigations showed increased colour changes for Logwood Maroon (from 0.38 to 0.41 $\overline{\Delta E}$) and Indian Yellow (from 3.09 to 3.52 $\overline{\Delta E}$) coloured samples with the sealant / UV-light absorber combination in comparison to the sealant only test samples; but colour changes decreased for non-pigmented specimens, Alizarin Crimson and Caucasian skin coloured specimens, the latter from 2.51$\overline{\Delta E}$ to 1.56 $\overline{\Delta E}$ and is illustrated in Fig. 6.22.

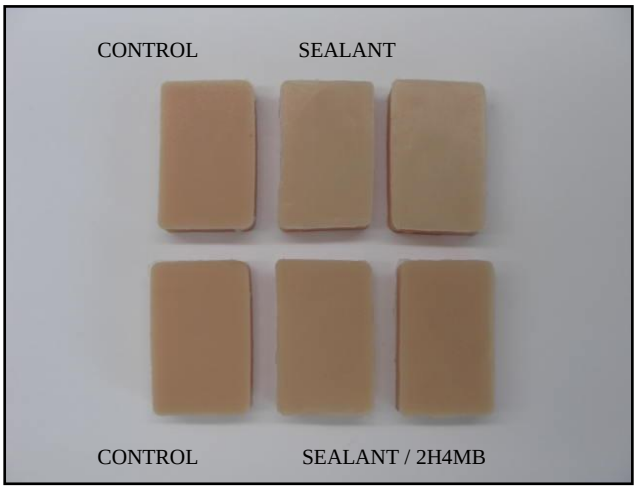


Fig. 6.22: Visual colour comparison of Caucasian skin control with Caucasian skin sealant and Caucasian skin sealant / UV-light absorber.

The results of this part of the study showed reduced colour changes for the majority of test groups with the protective surface sealant and incorporated 2H4MB UV-light absorber. Although the study by Beatty *et al*. (1999) cannot be directly compared with this current study, both investigations agree on colour change reducing effects when applying a silicone surface sealant. Although the calculated colour changes for Caucasian skin coloured test specimens were still perceivable, they represented a significant decrease of colour changes below the AT of 2 ΔE and are therefore clinically acceptable. The null hypothesis is therefore rejected for this part of investigations.

6.6.3.2. 2H4MB in combination with surface sealant: Effects of long term accelerated ageing

For fabrication of maxillofacial prostheses, elastomer is individually coloured with a variety of pigments in order to establish a good colour match between silicone and natural skin. Although colour changes of specimens with a protective surface sealant still slightly increased for some pigments when compared with

control samples; the results of the pilot study showed significant decrease of colour change for Caucasian skin coloured specimens.

Based on the results of the pilot study, further investigations were undertaken involving Caucasian skin coloured test specimens. Caucasian skin coloured control samples, samples with sealant only and samples with 1% and with 2% of 2H4MB were manufactured and exposed to accelerated ageing for a total of 1500 hours and results showed lowest colour changes for Caucasian skin coloured samples with sealant and 1% 2H4MB.

Application of the extrinsic silicone sealant only already improved the colour stability of skin coloured silicone samples when compared with non-treated control specimens; demonstrating $\overline{\Delta E}$ values of 1.99 (B) and 2.00 (W) compared to 3.25 (B) and 3.26 (W), respectively. It can be suggested that the applied silicone surface sealant shielded and protected the underlying Caucasian skin coloured elastomer and thereby reduced the degree of colour changes from non-acceptable to perceivable and still just acceptable clinical colour changes.

However, the additional use of either, 1% or 2% of UV-light absorber, reduced the overall colour changes after accelerated ageing for 1500 hours by nearly 50% when compared with non-treated control samples. Caucasian skin coloured specimens with sealant and 1% 2H4MB demonstrated lowest $\overline{\Delta E}$ of 1.18 (B) and 1.21 (W); and these colour change values are just perceivable and well within the AT of 2 ΔE (Fig. 6.22). Accelerated ageing for this test group and control samples was continued to a prolonged period of accelerated ageing for 3000 hours, and it was shown that the surface sealant and 1% 2H4MB further protected the silicone with $\overline{\Delta E}$ values of 2.03 (B) and 2.06 (W) in comparison to non-treated control samples with 5.38 (B) and 5.41 (W).

It can be suggested that protection and ‘shielding’ of the extrinsic surface sealant in combination with UV-light absorption provided by the 2H4MB particles located within the thin surface sealant layer both contributed to the much improved colour stability of Caucasian skin coloured M511 silicone elastomer.

Accelerated ageing for 3000 hours resulted in maximum colour changes of 2.06 $\overline{\Delta E}$ for samples with sealant and 1% 2H4MB which is just above the AT.

Based on the results of accelerated ageing for 3000 hours; if a facial prosthesis would be exposed eight hours a day to accelerated ageing, the obtained 2.06 $\overline{\Delta E}$ would be observed after 375 days. However, the effect of eight hours a day of accelerated ageing does not reflect the real life situation of facial prostheses, at least not in the British climate. It has been stated that natural outdoor weathering generally causes less colour changes than accelerated ageing in a weathering chamber and represents more closely the environment a facial prosthesis is exposed to in clinical service. Therefore, using this surface sealing technique should significantly prolong the life expectancy of facial prostheses.

Further research is now needed to investigate the effect of natural outdoor weathering on the colour changes of skin coloured maxillofacial elastomers. However, more precise estimates on the life expectancy of facial prostheses can only be achieved when testing this surface sealant / UV-light absorber technique under those conditions a facial prosthesis would be exposed to on a daily basis and should involve beside the influence of UV-light also humidity, air pollution and patient related factors including direct skin contact, prosthesis handling and cleaning measures as well as smoking. Considering this spectrum of environmental factors, in-vivo studies would be most effective and provide most realistic results; however, they are also most challenging to conduct.

Experiments in this current study involved investigations on the colour stability of Caucasian skin coloured elastomer; further research should include the colour stability testing of elastomer based on skin tones of other ethnic groups such as Asian and African, as different pigments would be used to establish these skin tones. However, in this pilot study, the UV-light absorber only was added to the extrinsic sealant. This application affects the overall colour and colour appearance of the skin coloured elastomer as 2H4MB particles are of light yellow colour. Application of this extrinsic sealant layer with 1% of 2H4MB resulted in a

translucent milky top layer on the base elastomer and makes the silicone appear ‘grey’ and different to the look of natural skin due to a lack of material opacity.

Research is now needed to use a skin colour recipe to colour the extrinsic sealant in the same way as the base elastomer was coloured and in combination with the 2H4MB UV-light absorber. Incorporation of the UV-light absorber into the sealant elastomer with a predetermined skin colour recipe will change the overall colour and therefore, colour formulation would be needed to compensate for the effect of the yellow colour of 2H4MB particles.

Clinical experience involves a frequent delamination of the extrinsic sealant layer from the main body of the facial prosthesis and consequently affects the overall colour and appearance of facial prostheses. Whereas this novel sealing method demonstrated promising results in order to protect the colour of facial prostheses and thereby their life expectancy; more research is needed to develop surface sealing techniques which provide a chemical bond between the base elastomer and the sealant to minimise the effects of delamination as known and frequently observed with currently available extrinsic sealant systems.

6.7. Conclusion

From the results of this part of the study it can be concluded that in comparison to non-treated control samples, the application of an extrinsic silicone surface sealant with incorporated UV-light absorber resulted in decreased colour changes of Caucasian skin coloured maxillofacial elastomer following accelerated ageing in a weathering chamber. The material combination of M511 silicone base elastomer coloured with Spectromatch Pro colourants, and the applied commercial extrinsic silicone sealant with added 2H4MB UV-light absorber demonstrated good overall colour stability in this in-vitro study with colour changes just above the AT of 2 ΔE following 3000 hours of accelerated ageing.

FINAL CONCLUSIONS

From the results of this study it can be concluded that M511 silicone elastomer coloured with pigments from the Spectromatch colouring system demonstrated visible colour changes as well as alterations of physical and mechanical properties when exposed to various environmental conditions. However, this silicone elastomer and pigment combination exhibited good overall colour stability and appropriate physical and mechanical strength and can therefore be recommended for use when manufacturing maxillofacial prostheses. Furthermore, a pilot study showed that the colour stability of skin coloured M511 silicone elastomer was improved by using a silicone surface sealant with incorporated UV-light absorber.

It can further be concluded that use of the Spectromatch Pro colour formulation software produced better colour match results between silicone and natural skin than did the traditional method of colour matching; and skin colour measurement utilising a spectrophotometer produced closest colour matches between elastomer and skin.

FUTURE RESEARCH

(i) Further work should address investigations to find more colour stable pigments which are also more resistant to environmental conditions including UV-light, changes in humidity and temperature, air pollution as well as personal habits and practices of patients. It should be aimed to conduct future research as in-vivo studies in order to imitate as closely as possible the natural environment facial prostheses are exposed to in clinical service.

(ii) The most colour stable pigments as identified in Aim 1 should be used to carry out in-vivo experiments on the physical and mechanical properties of elastomer in order to obtain detailed information on the life expectancy of maxillofacial silicone elastomer and consequently of facial prostheses in clinical service.

(iii) Based on the results from the pilot study on the application of a surface sealant with incorporated UV-light absorber in this research project, further experiments should be carried out to confirm its effect on improved colour stability of skin coloured elastomer. Experiments should also include in-vivo studies to mimic the situation where a facial prosthesis is worn by a patient.

(iv) The Spectromatch Pro colour formulation system was used in conjunction with a hand-held spectrophotomter and colorimeter for measuring the colour of natural skin. The degree of colour match between elastomer and skin may have been influenced by possible contact pressure between the measuring head aperture of the spectral instruments and skin during skin colour measurements. Further research should involve investigations on the use of contactless colour measurement systems in order to prevent the influences observed with hand-held skin colour measurement devices.

(v) The functionality of the Spectromatch Pro colour matching software was only used with pigments in this current study; further work should include the use of flocking as colourants to see whether this will improve the degree of colour match between silicone elastomer and natural skin.

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APPENDICES

Appendix A: Reported PT and AT in textile/paint industry and dentistry

Year of publication	Author(s)	Application / investigations	Statement for PT and / or AT
1979	Kuehni and Marcus	Textile and paint/ relationship between calculated colour difference values and human observer responses coloured textile and cardboard samples	ΔE of 1 perceived by 50 % of observers
1989	Seghi *et al.*	Dentistry / relationship between calculated colour difference values and human observer responses involving translucent dental porcelain	ΔE of 1 perceivable by average group of dental observer; ΔE of 2 correctly judged by 100 % of observers
2001	Ragain and Johnston	Dentistry / visual assessment of colour differences using monochromatic composite resin disks	AT of 2.7 ΔE
2007	Wee *et al.*	Dentistry / visual assessment of colour differences using monochromatic porcelain specimens	PT of 1.2 and AT of 1.6 ΔE
2007	Douglas *et al.*	Dentistry / visual assessment of colour differences using polychromatic denture teeth	PT of 2.6 and AT of 5.5 ΔE
2007	Lindsey and Wee	Dentistry / visual assessment of colour differences in computer simulated teeth	Observer sensitivity to 1.25 ΔE in L* and a* direction of colour space, and 2.6 ΔE in b* direction; no difference between PT and AT
2010	Lindsey and Wee	Dentistry / visual assessment of tooth colour differences in digital facial portraits	Observer sensitivity to ΔE range of 1.45 to 2.9; similar to results of Lindsey and Wee (2007)
2015	Paravina *et al.*	Dentistry / visual assessment of colour differences involving 50:50% PT and AT of dental ceramic with medium to light shades, medium to dark and dark shades	CIE L*a*b* 50:50% PT of 1.2 ΔE and AT of 2.7 ΔE

Appendix B: Colour formula for Caucasian skin tone

Components of Caucasian Skin Tone: summary of used pigments / elastomer and the equivalent loading, given in percent (%).

Pigment / Elastomer	Pigment / Elastomer Loading (%)
Titanium White	0.59
Indian Yellow	0.02
Alizarin Crimson	0.05
Goethe Brown	0.04
Academy Blue	0.01
M511 Part A	90.26
M511 Part B	9.03

Appendix C: Summary of weather data

A summary of recorded daily weather data in London / Heathrow for the period of outdoor weathering in this current study was provided by the Met Office and can be found on the CD enclosed with this thesis.

Appendix D: Colour stability testing data

All colour measurements and calculated $\overline{\Delta E}$ of all test samples and for all test groups is provided on the CD enclosed with this thesis.

Appendix E: Physical and mechanical properties testing data

A summary of physical and mechanical properties testing data of all test samples and for all test groups is provided on the CD enclosed with this thesis.

Appendix F: Ethical approval letter

The ethical approval letter is provided on the CD enclosed with this thesis.

Appendix G: Flow chart of research methodology

A flow chart of the study is provided on the CD enclosed with this thesis.

Appendix H: Information sheet for participants

Version 2 of the information sheet for participants is provided on the CD enclosed with this thesis.

Appendix I: Consent form

The consent form for participants is provided on the CD enclosed with this thesis.

Appendix J: Results of colour deficiency test

The results of the colour deficiency test for participating colour assessment judges are provided on the CD enclosed with this thesis.

Appendix K: Summary of skin colour matching data

All data of skin colour measurements, silicone elastomer colour measurements, colour difference calculations and results of visual colour match assessments is provided on the CD attached with this thesis.

Appendix L: Summary of minimum and maximum ΔE for spectrophotometer and colorimeter

A summary of minimum and maximum ΔE values for both instruments, overall and per ethnic group is shown in Table 1. The minimum and maximum ΔE values in relation to elapsed time, overall and per ethnic group, are shown in Figs. 1 to 4.

Instrument	$\overline{\Delta E}$	overall	C	A	AfC
Sp	min	0.42	0.49	0.49	0.42
	max	7.32	7.32	5.34	6.06
Col	min	0.18	0.41	0.45	0.18
	max	7.15	7.15	4.83	4.73

Table 1: Minimum and maximum $\overline{\Delta E}$ for both instruments, overall and per ethnic group.

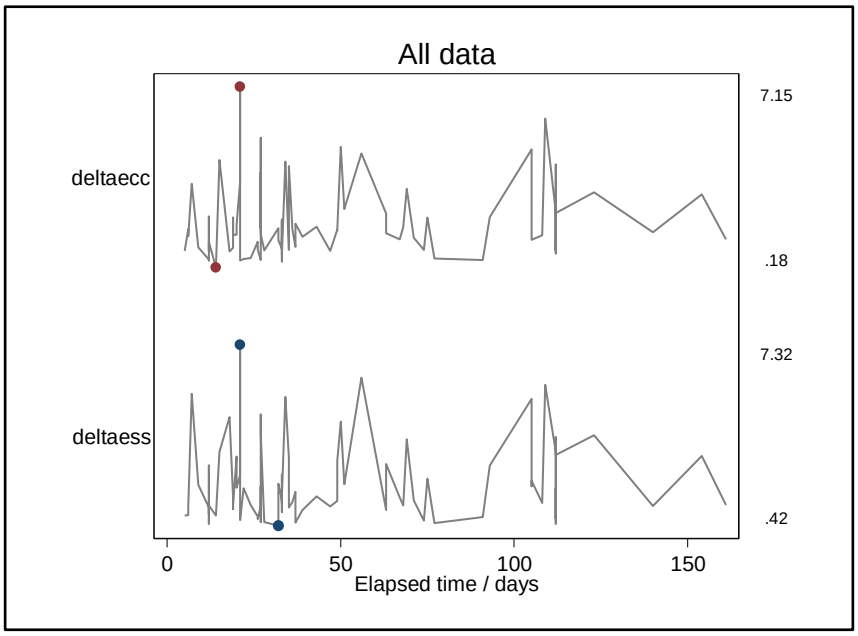

Fig. 1: $\overline{\Delta E}$ for each instrument in relation to elapsed time, overall.

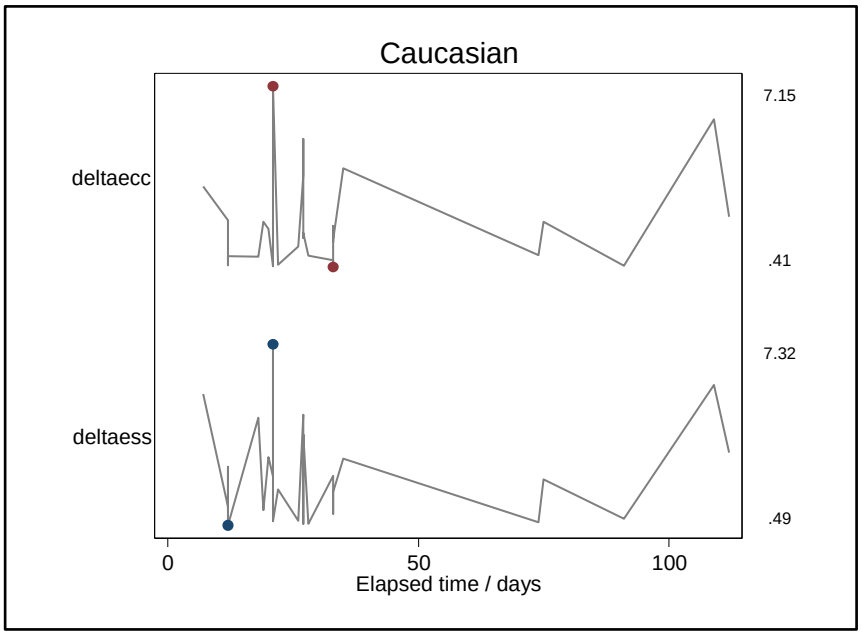

Fig. 2: $\overline{\Delta E}$ for each instrument in relation to elapsed time, Caucasian ethnic group.

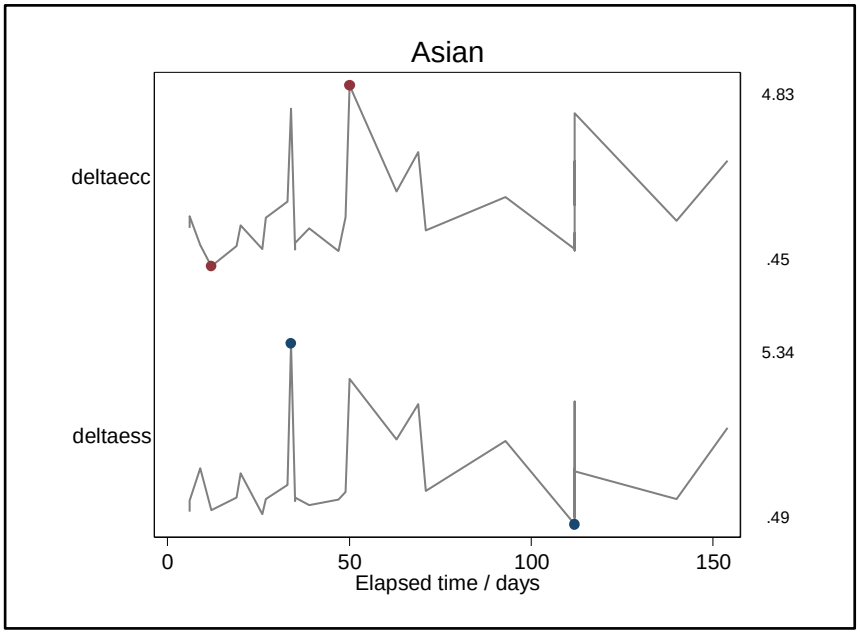

Fig. 3: $\overline{\Delta E}$ for each instrument in relation to elapsed time, Asian ethnic group.

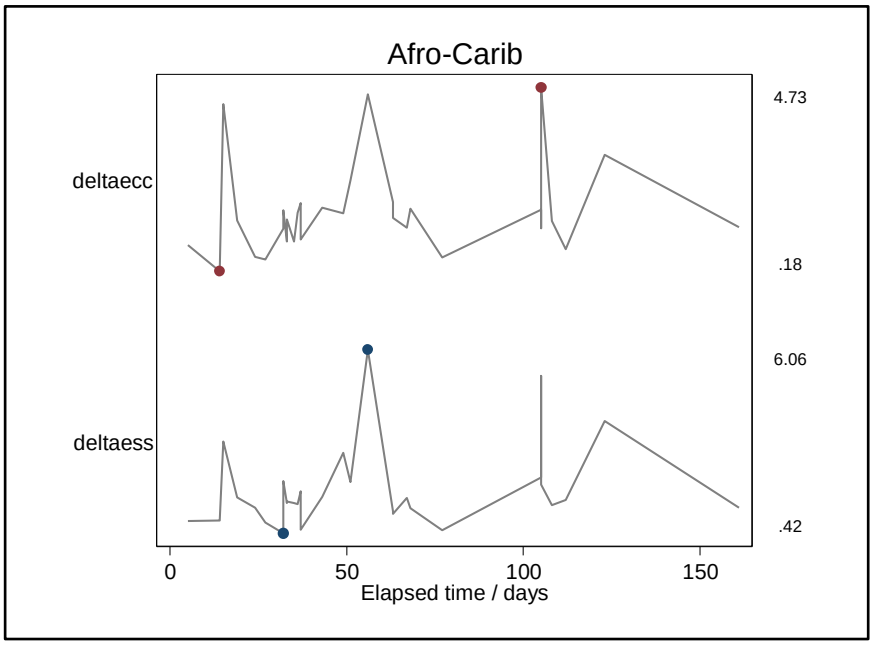

Fig. 4: $\overline{\mathbf{\Delta E}}$ for each instrument in relation to elapsed time, Afro/Afro-Caribbean ethnic group.

Appendix M: Summary of data on surface sealant and UV-light absorber experiments

A summary of all data for experiments involving surface sealing of silicone and the use of UV-light absorbers is provided on the CD attached with this thesis.

Appendix N: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period for use of UV-light absorbers

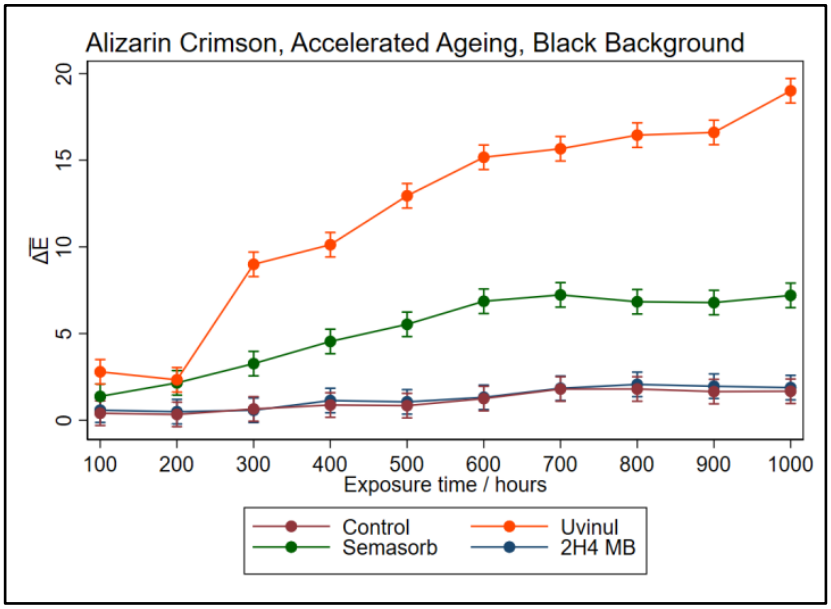

Fig. 5: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

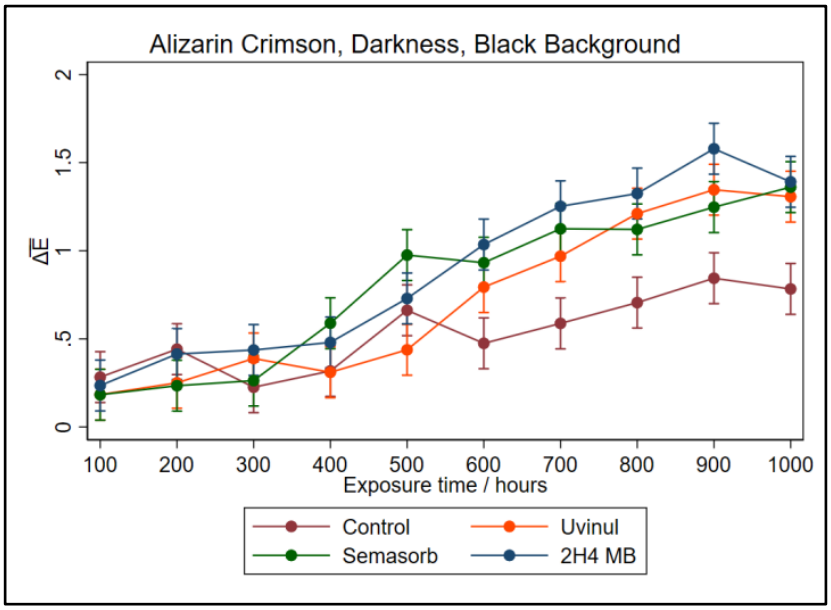

Fig. 6: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

Appendix O: $\overline{\Delta E}$ values and associated 95% confidence interval for Parylene coating and silicone mixing in nitrogen environment

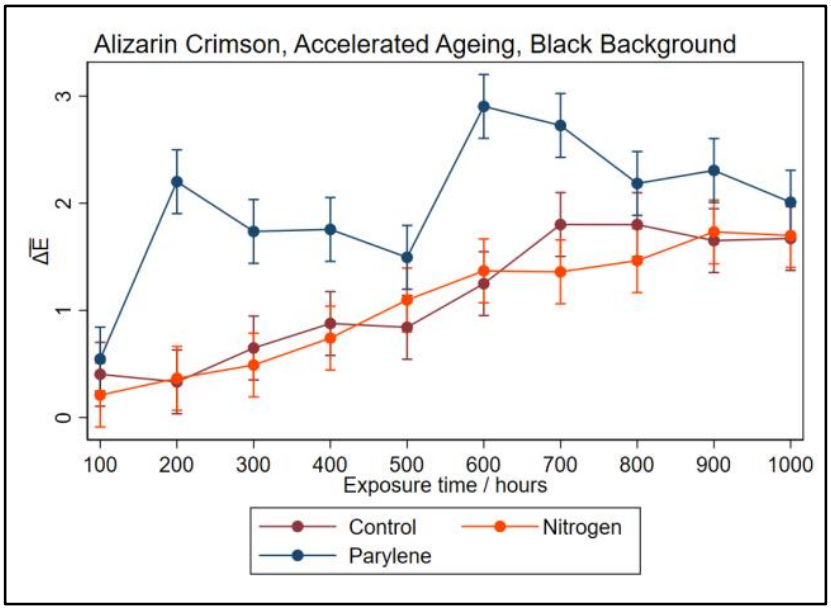

Fig. 7: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

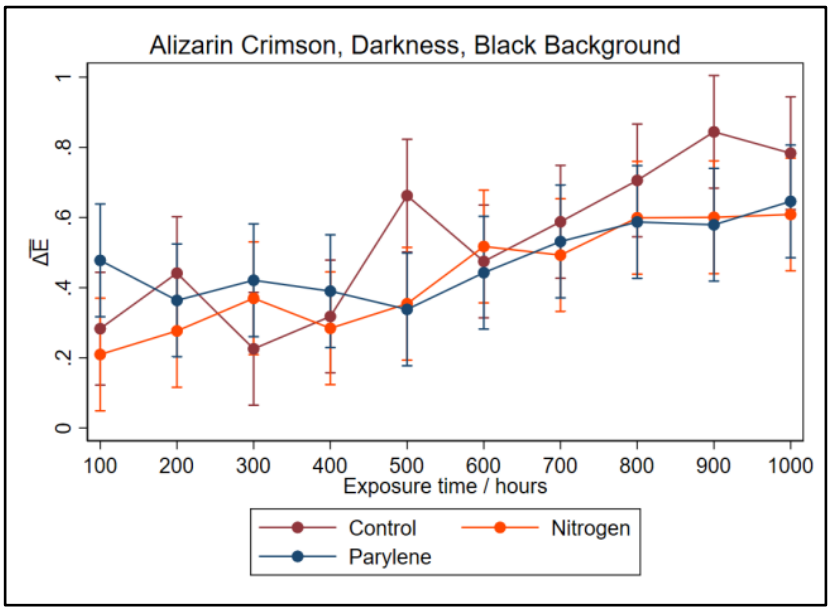

Fig. 8: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

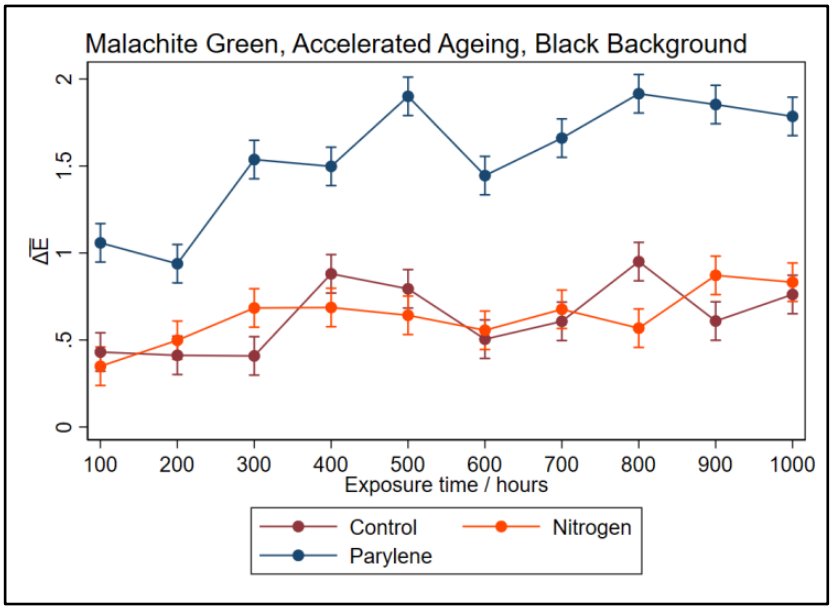

Fig. 9: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

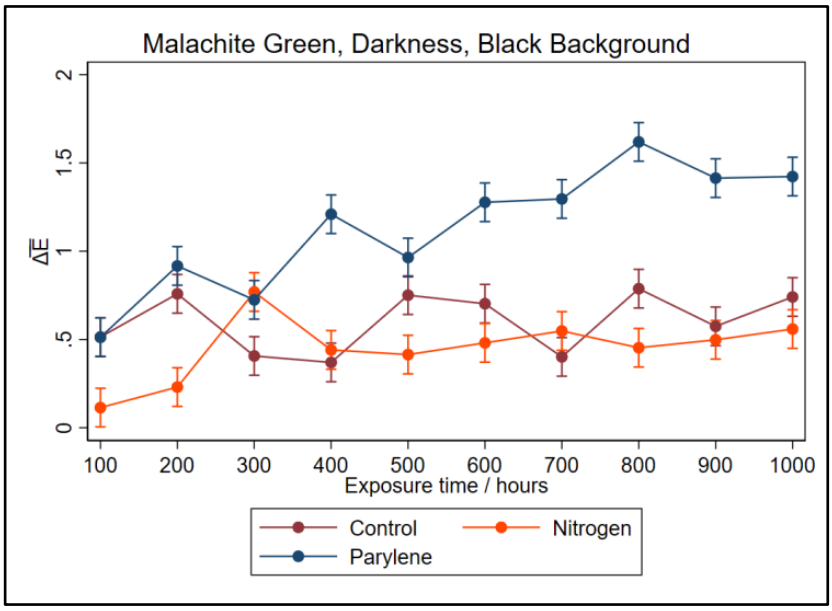

Fig. 10: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

Appendix P: $\overline{\Delta E}$ values and associated 95% confidence interval for experiments involving surface sealant

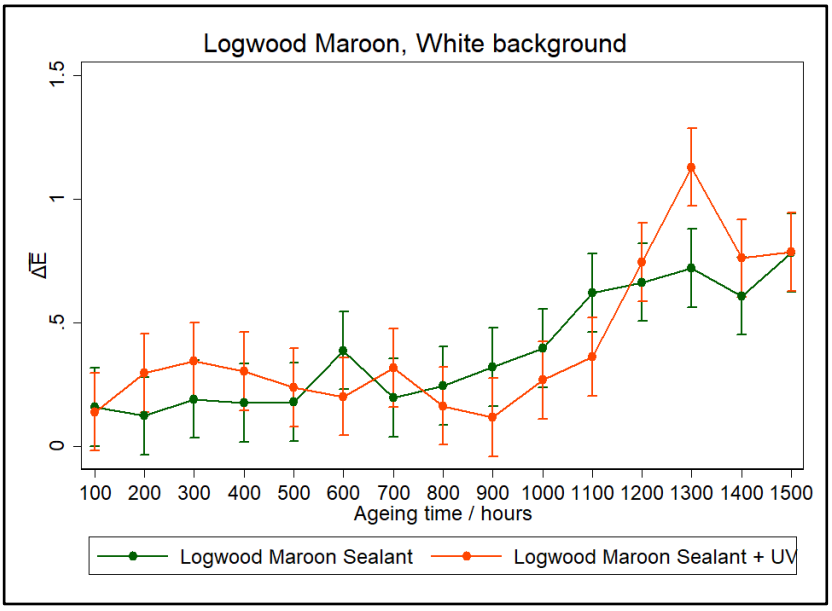

Fig. 11: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

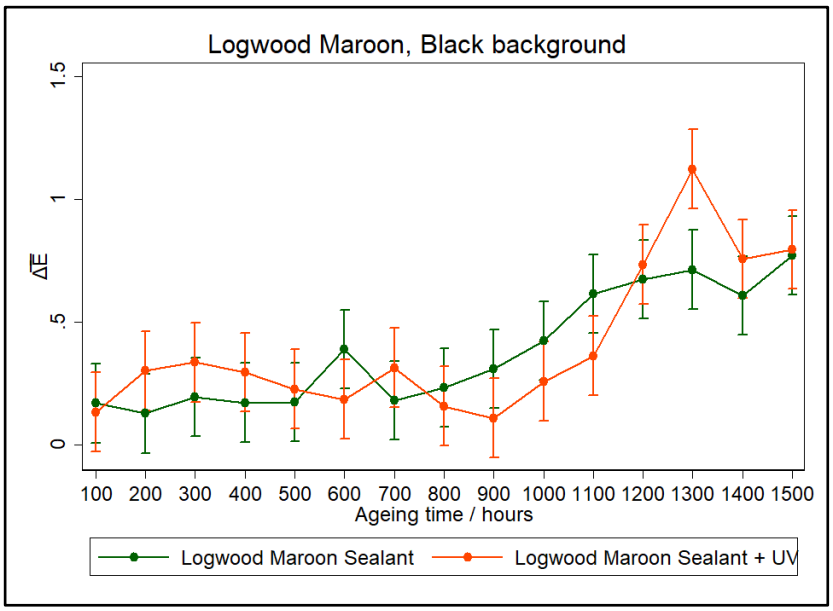

Fig. 12: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

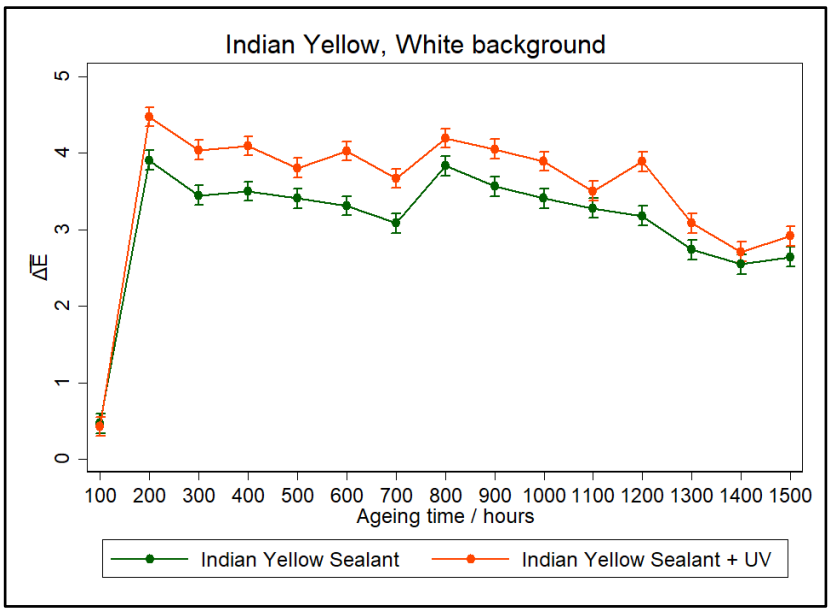

Fig. 13: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

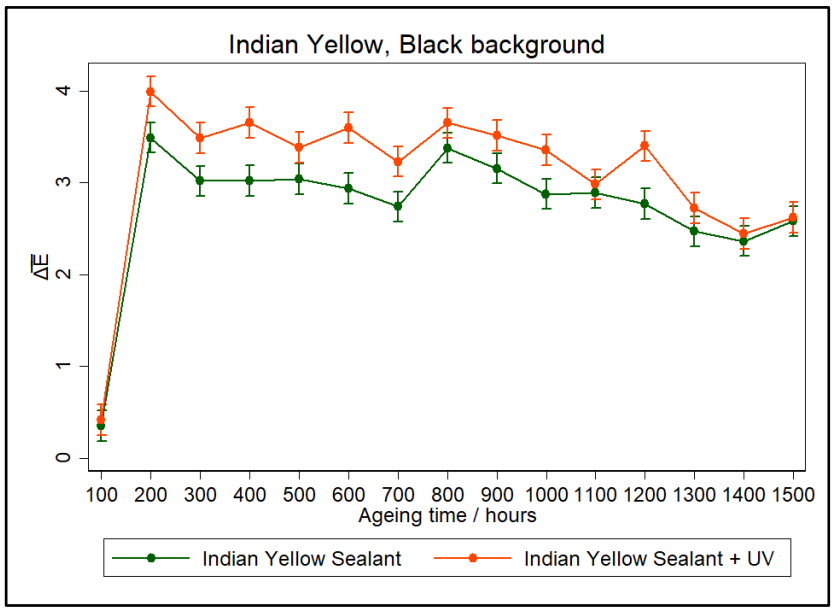

Fig. 14: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

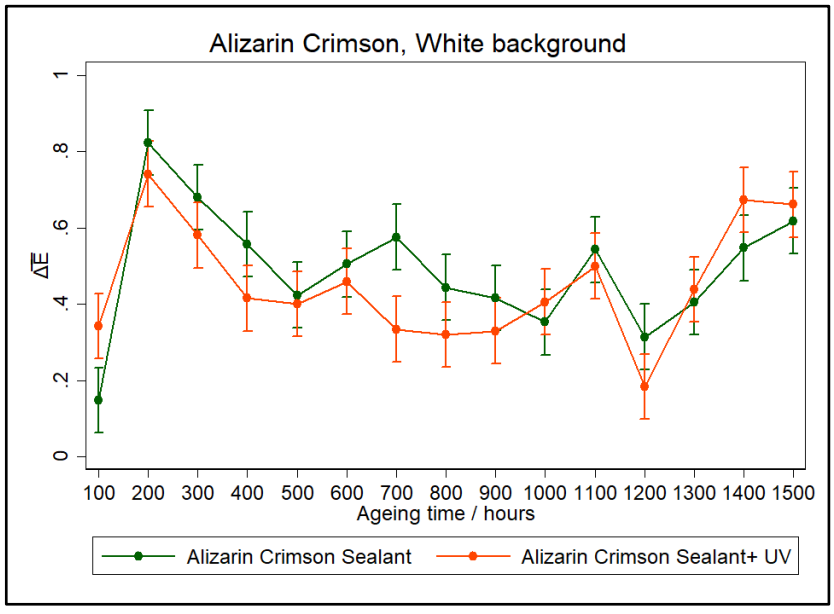

Fig. 15: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

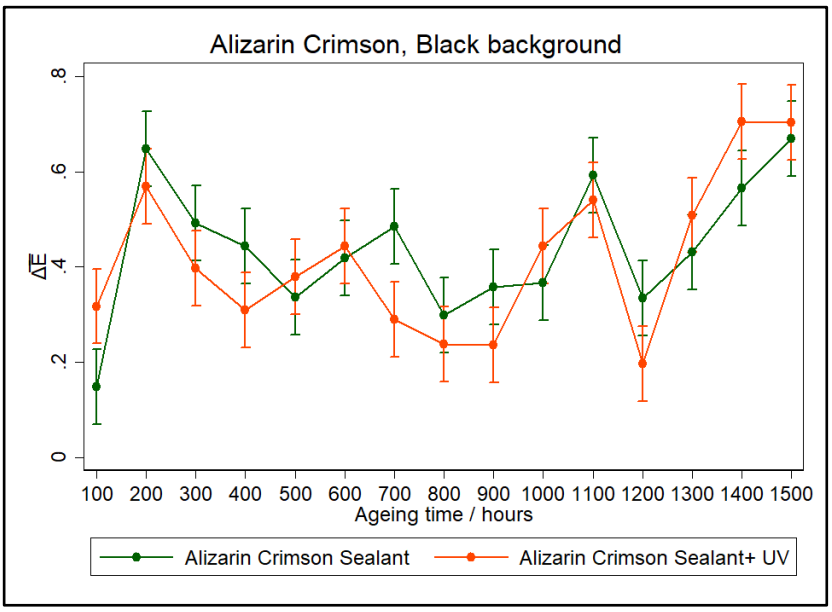

Fig. 16: $\overline{\Delta E}$ values and associated 95% confidence interval at each time period.

LIST OF MANUFACTURERS AND SUPPLIERS

BASF SE

Carl-Bosch-Straße 38

67063 Ludwigshafen am Rhein

Germany

Carbolite, Thermal Engineering Services

PO Box 2033

Hope Valley

S33 6XY

UK

Hauschild Engineeering

Waterkamp 1

59075 Hamm

Germany

Instron

Coronation Rd

High Wycombe

HP12 3SY

UK

Konica Minolta Sensing

3-91 Daisennishimachi

Sakai-ku, Sakai

Osaka, 590-8551

JAPAN

Mettler Toledo Limited

64 Boston Road

Beaumont Leys Leicester

LE4 1AW

UK

Microsoft

Microsoft, Headquarters

1 Microsoft Way

Redmond, WA

USA

Q-Panel Lab Products

26200 First Street

Cleveland, OH

USA

Sauter GmbH

Ziegelei 1

72336 Balingen

Germany

Se ma Gesellschaft für Innovationen mbH

Industriestraße 12

06869 Coswig (Anhalt)

Germany

Sigma-Aldrich Chemie GmbH

Eschenstraße 5

82024 Taufkirchen

Germany

Specialty Coating Systems (SCS)

Kingswey Business Park, Forsyth Rd

Woking GU21 5SA

UK

Spectromatch Limited

23 Thames St.

Hampton

TW12 2EW

UK

Stata Corporation

Stata Statistical Software

College Station, Tx

USA

Technovent Limited

5 York Park

Bridgend

CF31 3TB

UK